

VARNISHES AND
THEIR COMPONENTS

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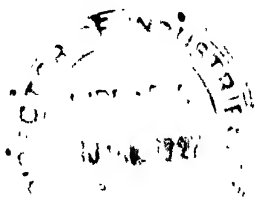
VARNISHES AND THEIR COMPONENTS

BY

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LONDON

HENRY FROWDE AND HODDER & STOUGHTON

THE LANCET BUILDING,

1 BEDFORD STREET, STRAND, W.C.2

First printed 1923.

Printed in Great Britain by R. & R. CLARK, LIMITED, Edinburgh

PREFACE

THE object of this book is to present a summary of the recent advances in the study of varnishes and their components. A detailed treatment worthy of the importance of the subject is impossible in a volume of comparatively small size, but those who wish to obtain instructions for the carrying out of the processes on a factory scale will find references to reliable authorities. For the convenience of readers who are unable to consult the foreign authorities, abstracts will be found in the *Journal of the Society of Chemical Industry*, and in the bibliography at the end of this book.

It has been considered necessary to lay stress on the chemical composition of the components of varnishes as far as they are known to affect the properties of the "mixings." It must be confessed that the influence of chemical composition often appears feeble, but in the opinion of the writer closer investigation always maintains the connection between chemical composition and properties.

The varnish-maker deals for the most part with substances of a colloid nature which give systems whose properties are often not comparable with those of colloids in aqueous media. The composition of linseed oil, which is the most important component of oil varnishes, is fairly well known, but the "drying" or oxidation process has been very inadequately investigated. As in paints the oil medium is one of the decisive factors of the durability of the coating, although in varnishes the durability is greatly influenced by the amount and quality of the resins, which themselves have been also inadequately investigated. The properties of linoxyn and the changes which occur on the weathering of resins dissolved in drying oils would form excellent subjects for investigation by a Research Association. I have laid stress on the consideration of problems of viscosity and elasticity in the maintenance of uniformity throughout the varnish film, which is of paramount importance in producing a permanent plane surface and in preventing "bloom." The presence of small quantities of foreign substances profoundly modifies the superficial properties of varnish films, which

is a characteristic of colloid systems, and many such changes cannot be easily explained. Nevertheless, from the author's experience the properties of varnishes conform broadly to those of normal systems, if due allowance be made for the special relationships of the components.

Readers may be disappointed in not finding recipes for the preparation of up-to-date varnishes. The formulæ given illustrate general principles without going fully into craftsmen's details. Even if full details were given, variation in the quality of the raw material would seriously affect the qualities of the products. There are, however, a few principles connecting the proportions of the components, and if good results are required good materials must be used. I have lightly touched on the details of the decorator's craft, and on the essential importance of undercoats of good quality, because many of the superficial defects are caused by neglect of the preparation of the under-surface.

The chapter on spirit varnishes contains a short reference to "dopes" or soluble cellulose spirit mixings, which are still used as rather inadequate protectors of metals.

The large demand for insulating varnishes has merited a special chapter. Linoleum has not been included, although a study of the processes of that industry is of value to any interested in the properties of linoxyn. A summary of the knowledge of this industry has been given by de Waele and the writer in *Rubber, Resins, Paints, and Varnishes*.

My thanks are due to Messrs. Mander Brothers, Wolverhampton, for permission to publish this book; to Dr. Morgan and Mr. Hedley Barry for kindly reading the proofs, and for making many helpful criticisms; to Dr. V. Eyre for photographs of varieties of linseed; to the British Engineering Standards Association for permission to reproduce the details of many specifications; to the Aerostyle Company (Spraying Apparatus), the Aluminium Plant and Vessel Company (Jum Melting Pots), Messrs. Goodyear of Dudley (Stoves), Messrs. S. H. Johnson (Filter-presses), Messrs. Scott, Ltd. (Extraction Oil Plant), the United Water Softeners Company (Sharples Centrifuge), and to the Editor of the Oil and Colour Chemists Association, who have supplied blocks for some of the illustrations and useful descriptive details. Last but not least, I wish to express my indebtedness to my wife for the labour of typesetting the mass of details involved in the compilation of the MS.

R. S. MORRELL

WOLVERHAMPTON.

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HISTORICAL INTRODUCTION

PRIOR to the 9th Century the term "varnish" was applied to a resin. The *Oxford English Dictionary* (1916) gives the variations of the word from the 14th to the 17th Century: English, *vernisshe* (14th Century), *vernyshe* (15th to 17th Century); Old French (12th Century), *vernīs* or *verniz*; Middle High German, *firnīs*; Mediæval Greek, *βερνίκη*; Spanish, *barniz*.

References to it are described in lb. weight, whilst fluids such as oils are stated in gallons. In the accounts for the decoration of the Painted Chamber at Westminster in 1274-77 the following items appear:

To Reymond—17 lb. white lead . . .	IIs Xd
24 lb. varnish . . .	XIIIs
16 gallons oil . . .	XVIs

The varnish melted and boiled with linseed oil formed a liquid, *vernice liquida*. The Greeks gave to amber the name *berenice*, as they considered that it resembled in colour and lustre the sacred yellow locks of Berenice, Queen of Cyrene (3rd Century A.D.). Berenice (*pheronice*, "who gives victory") became *verenice*, *verniz*, and *vernīs* (Mediæval Latin).* *Veronice* or *verenice* was the common name for amber in the MSS. of the Middle Ages. After the 16th Century the word *vernix* ceased to be applied exclusively to dry resin and was used to denote a fluid compound. The legendary origin of the word *varnish* as being equivalent to amber has been put forward by some writers, but it does not seem to be entirely satisfactory, and according to the *Oxford English Dictionary* (1916) the origin of the word is unknown. The Egyptians made a good varnish composed probably of soft resins or oleoresins and possibly linseed oil, but without thinners. It is stated by some that the Egyptians were entirely unaware of the oil that could be expressed from linseed. It is possible that the resins contained copals from the interior of Africa, and since flax was cultivated in Egypt the oil most probably was linseed oil. The varnish found on mummy cases is in excellent preservation, and must have been applied with the finger or with a spatula. Many of the softer resins from the East, e.g. sandarach, mastic, and olibanum, must have been available to the ancients.

* The German name for amber is *bernstein* (Berenice's stone).

The resins were applied in the form of a powder, which was melted by holding a hot iron or torch near them, after which the surface was polished by rubbing. The application of varnish to paintings and the polishing of sculpture by rubbing in resins were practised by Apelles and Praxiteles. Soft resins such as mastic, sandarach, and olibanum were used (the word libanum is found in the poems of Leonides, 3rd Century B.C.). Pigments were mixed with melted wax and applied in liquid form with a brush; when cold the surface was re-melted to produce an apparently enamelled surface, or the coloured wax in the solid form, closely resembling wax crayons, was applied to a warmed surface with a tool known as a *cauterium* and modelled into shape (Laurie, *Materials of the Painter's Craft*, 1910, p. 55). The effect was enhanced by mixing resins with the wax to harden it, or by applying resin to the surface and so forming a varnish finish.

Chaucer, "The Reeve's Tale" (1386):

Wel hath the myller vornysshed his heed,
Ful pale he was for, dronken and nat reed.

The use of oil as a solvent for resin is mentioned by Pliny, "resina omnis dissolvetur oleo," and, before Pliny, Dioscorides described walnut and poppy oil, which are also drying oils.

The principles of varnish-making in Europe were first put forward by Theophilus Presbyter (probably Tutilo of St. Gall, 10th-11th Century A.D.), who in his "Schedula Diversarium Artium" gave recipes of standard and well-known technological processes. The manufacture of an oil varnish is here described for the first time. It was made from "oleum and gum fornis" by melting the gum and dissolving in hot linseed oil, heating until one-third of the mixture had been sweated off, and adding more hot oil until the proportions of oil to resin were two to one. The product was tested during the making in much the same manner as now. The resin used was amber. The varnish was not thinned, and was applied warm by the finger rather than by brush. In 1388 a similar formula was put forward by Alcherius. In 1520 rosin (*pica greca* or *gloriat*) was mixed with sandarach and run in linseed oil to give a varnish for armour, cross-bows, and arquebuses, and applied by a sponge or a piece of wood, but no thinners were added. Ordinary varnish used from the 9th till late in the 15th Century consisted of a fairly soluble resin—sandarach or mastic, or both, dissolved in linseed oil, with the addition, in many cases, of a considerable quantity of rosin. In 1575 mention is again made of the running of amber in oil, a small quantity of oil being employed at first, and afterwards the rest of the oil was added on the lines of the recipe given by Theophilus. It is not until 1750 that Alberti of Magdeburg described the manufacture of an amber linseed oil varnish thinned with turpentine. These oil varnishes were made on a very small scale, 6 oz. of amber per melt being used compared with 120 lb. of resin per melt nowadays. The varnishes were of the long-oil class and the driers were lead and umber (Petitot of

Geneva, 1644). The use of driers in vegetable oils has been known for centuries. Galen (2nd Century A.D.) and Marcellus (4th Century A.D.) mention the use of lead and umber in the drying of oils. The use of manganese as a drier is comparatively recent. Faraday in the early part of the last century is credited with its use on purely theoretical grounds. The bleaching of oils by sunlight is mentioned by Dioscorides. Poppy and walnut oils are described by him, but not linseed oil, the use of which is not mentioned before Actius (5th Century A.D.). The mediæval painters were most careful in the purification of the oils used. Water seemed necessary in the refining of oils, and the two were heated together for several days to dissolve out soluble ingredients, the mixture then being allowed to settle and the oil poured off. The addition of anhydrous salts to remove the water brought in the use of white vitriol (copperas). There is no doubt that the use of this substance originated from the old custom of refining, and the classification of copperas among "driers" was based on a misunderstanding of terms; although in an impure state, containing manganese, it would accelerate the drying of linseed oil.

The preparation and filling of the wood previous to painting as recommended by Theophilus and Cennini (14th Century) have a close resemblance to the craftsman's methods of to-day. Jan van Eyck's pictures (1410) probably owe their durability not merely to the colours incorporated with the oil, but to the use of an oleoresinous vehicle such as might be strictly employed, as a varnish over a finished picture. Nevertheless he may not have painted in oil and may have glazed his pictures, begun in tempera, with a medium containing some oil to increase their permanence and brilliance (Laurie, *loc. cit.* p. 375).* The Flemish painters Cuyt and Rembrandt are said to have used an oleoresin varnish as a vehicle, and the latter employed an amber varnish. Leonardo da Vinci (1515) is stated by Vasari to have used a similar vehicle. The use of such oleoresin vehicles made a final varnishing unnecessary; nevertheless the use of varnish has again given place to oil, although modern paintings do not equal those of the mediæval masters in durability. The variety of pigment colours is now much greater than formerly, and the result of mixing varnish with the oil colours is often unsatisfactory.

Watin in 1773 is the first author to write on paint and varnish as now used technically. Copal and amber were the two principal resins employed, copal being reserved for the paler varnishes and amber for gold varnishes or those used over dark colours. The resins were previously sweated before incorporation in the oil, which was as pale as possible and well clarified. Turpentine was employed as a thinner, and without it the varnishes are stated not to have dried. The smaller the amount of oil the harder and quicker drying was the varnish; 1 lb. of copal was used with a quarter or half a

* Venice turpentine and oleo di abbezzo (the balsam of the silver pine) were used, with little admixture of oils, as media, in the time of Van Eyck and his immediate followers.

pound of oil. The first varnish factory was established in England in 1790, in France and in Germany between 1820 and 1830, followed by Austria in 1843. The manufacture of varnish in America was on a comparatively small scale twenty or thirty years ago, but nowadays it is a serious competitor with England and Germany in the matter of production. England and Holland were the first to put varnish manufacture on a technical basis.

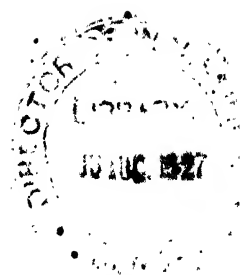
Tingry (1803) describes five classes of varnishes: two classes of spirit varnishes, one class of turpentine varnishes, one class of soft copal varnishes containing oil of lavender as solvent with the addition of 2 per cent of camphor, and one class of oleoresinous varnishes containing copal or amber, linseed or nut or poppy seed oil, with turpentine as thinner. The quantity of varnish prepared in one operation was very small, and Tingry recommends that not more than 6 oz. of resin should be incorporated with oil at any one time. Wilson Neil (*J. Soc. A.* vol. ii. p. 49) gave a detailed account of the actual operation of melting resin and combining it with oil and turpentine. The quantities of resin and oil used by him in one operation were still small, viz. 8 lb. resin and 2-3 gallons of linseed oil. For details of the various processes references may be made to Mackintosh, *Varnish Materials*, vol. ii. p. 118. It must be admitted that progress since Wilson Neil's publications has been slow. The varnish industry has been hampered by empiricism, which was largely due to the entire lack of knowledge of the properties and composition of the component materials. This empiricism produced a vast number of trade secrets, which are the craftsman's delight and the bewilderment of the student. Great confusion often arose because of inexplicable changes in conditions due to the employment of new material. The chemistry and physics of varnish-making are complex, the media are non-aqueous, and the chemical changes require most careful study, especially in the presence of substances of a colloidal nature in media, which have up to the present been only very slightly investigated from a colloid point of view. The superficial properties often seem to have a remote dependence on chemical composition, although careful research gradually indicates a connection, the establishment of which greatly facilitates the technology.

No historical introduction can be complete without reference to the rise and development of the Chinese and Japanese lacquer industry. In the Far East, in China and in Japan, lacquer work was known from time immemorial. Though tradition says that it was known in Japan as early as the 4th Century B.C., it is supposed that the art came originally from China. In Japan a State department for lacquer work existed in 392 A.D., and in the 7th Century lacquered articles were received in payment of taxes. At first its uses were purely utilitarian. Drinking vessels were coated with lacquer to render them water-tight, and as the surface was as hard as glass and withstood considerable heat, it was used largely for cooking and other household utensils. The slow development of the potter's art in Japan is considered to be due to lacquered

vessels taking the place of glass and earthenware. The Japanese warrior often wore leather coated with lacquer as armour; his sword was in a lacquered scabbard; he ate off a lacquered tray, drank out of a lacquered cup, and rode in a lacquered carriage. Stewart Dick, *Arts and Crafts of Old Japan*, states that the earliest examples of lacquered work preserved date from the 6th and 7th Centuries, and by the 10th Century some very fine work had been produced. In A.D. 1500, Chinese methods were introduced into Japan, and in the 17th Century the period of the great lacquer workers set in. The period of Tokugawa Shogun Iyeyasu marked the highest point of excellence.

The process of lacquering was long and tedious, the number of operations required in the production of a piece of plain ornamented black lacquer being no fewer than thirty-three; while for the production of one of the more elaborately ornamental pieces the number might reach sixty or more. To quote Stewart Dick again: "The most wonderful of all the Japanese arts is their lacquer work; and, perhaps, in this more completely than in any other medium does the peculiar genius of Japan find expression. Even were the same brilliant faculty of design the gift of the European, the amazing and unflinching precision of hand and the limitless patience and unceasing care required by the technical processes, place lacquer work far beyond his scope. It is only the Eastern who can combine the imagination of the artist with the technical powers and steady perseverance of the ant or the bee." To one who has seen specimens of the finest work (the glorious lacquer of old Japan) the words of the French critic Louis Goussier appear no more than a mere statement of fact: "Japanese lacquered objects are the most perfect works that have ever issued from the hands of man." The traditions of the craft were hereditary, and retained in certain families. The Komas were Court lacquerers for more than two hundred years, the first of the family, Koma Kiui, who died in 1663, being lacquerer to the Shogun Iyemitsu. Of modern masters the most famous is Zeshin (1807-91), and his work is worthy to rank with his great predecessors.

Modern industrial conditions do not admit of the same patient workmanship—months and perhaps years being expended on one article. A quicker drying lacquer is required, and as a consequence this has neither the lustre nor the durability of ancient material. A memoir by D'Incarville, a French Jesuit missionary of the 18th Century, contains a full description of the mode of collection of the lac. Specimens of really fine lacquer are rarely to be seen outside Japan, where they are treasured in the collections of the wealthy. In England there are a few fine private collections, but in the British Museum and at South Kensington only a few small pieces are to be seen. Possibly the supply of lacquer will be increased because of its general protective value, and the artistic work will again become popular in the Western World.



PART I

THE COMPONENTS OF VARNISHES

CHAPTER I

DRYING OILS

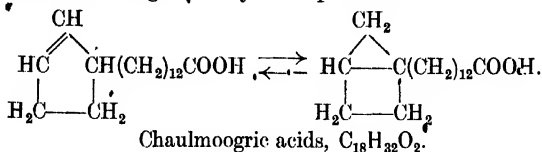
THE oils which a varnish maker uses show the property of "drying" in the air. The difference between drying and non-drying oils can be shown by comparison of the behaviour of petrol, white-spirit petroleum, kerosene or paraffin oil, olive, castor, and linseed oils. If plates be coated with thin films of these liquids and exposed to the air for several days, it will be found that the petrol and the white spirit have evaporated completely; the kerosene will have partly disappeared, leaving a considerable amount of greasy residue; olive and castor oils will be unchanged, but the linseed oil coating will have become tacky and will finally set to a tough, varnish-like film. The petroleum oils contain volatile and non-volatile components at the ordinary temperature, just as turpentine oil does, whereas castor and olive oils remain greasy and apparently unaltered, but linseed oil becomes viscous and sets to a soft, tough film. Olive and castor oils are typical non-drying oils, and their viscosities change only slightly on exposure to air. Linseed oil is a typical drying oil. The semi-drying oils will become tacky very slowly, and only on prolonged exposure do they yield flexible films.

The property of drying can be accelerated, in the case of drying oils, by addition of driers, to which reference will be made in a special section. In spite of the vast quantities of linseed and other drying oils handled annually, the changes which occur during the drying process are not fully understood.

The general properties of linseed oil may be considered typical of the class of vegetable drying oils, and a detailed account of its properties, with due consideration of differences in composition and orientation of component atoms, will apply to all the most important drying oils.

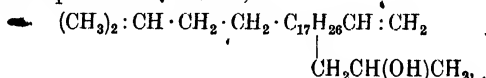
Linseed oil contains the triglycerides of unsaturated acids of the aliphatic series, with eighteen carbon atoms in an open chain.

It is of interest to note that no open-chain drying oil of vegetable origin is known containing less than eighteen carbon atoms, with the exception of the glyceride of isonic acid ($C_{14}H_{26}O_6$). The majority are open-chain compounds, with the exception of the oils from chaulmoogra and hydnocarpus seeds.¹



As glycerides the drying oils are saponifiable in contradistinction to mineral oils, which are unsaponifiable. They may be termed fixed oils in that they cannot be volatilised under atmospheric pressure without decomposition. The drying oils of animal origin, *e.g.* menhaden and Japanese fish-oil, contain the triglyceride of clupanodonic acid,² $C_{22}H_{34}O_2$, whilst the liver oils of certain members of the shark and dog-fish families contain spinacene,³ $C_{29}H_{48}$, a highly unsaturated hydrocarbon, which Tsujimoto⁴ regards as identical with squalene, $C_{30}H_{50}$, present in the oil obtained from the livers of two Japanese sharks, Ai-Zamé and Heratsuno-Zamé (*vide* fish oils).^{*} These hydrocarbons are unsaponifiable, and when exposed to air form hard skins similar to those given by linseed oil. Spinacene forms a dodecaboride $C_{29}H_{46}Br_{12}$.

A characteristic difference between animal and vegetable oils, including drying oils, is that the former contain cholesterol, $C_{27}H_{46}OH$, probably a terpene of the formula,⁵



which is a component of the well-known lanolin, whereas the phytosterols (sitosterol), $C_{27}H_{46}O$, are found in all fats and oils of vegetable origin. The recognition and properties of these components is a matter of importance which will be referred to under the section on the examination of drying oils.

LINSEED OIL

Genuine linseed oil contains essentially the triglycerides of linolenic, linolic, and oleic acids, which are present as mixed glycerides of slightly variable composition, depending on the source of origin and on the maturity of the seed from which the oil is expressed. The general formula of the glycerides may be

represented by the scheme $\begin{array}{c} \text{OL} \\ \diagup \quad \diagdown \\ \text{C}_3\text{H}_5 - \text{OL}_1 \\ \diagdown \quad \diagup \\ \text{OL} \end{array}$, where L, L_1 , and OL are the

^{*} Squalene contains six double linkages, and gives with hydrochloric acid a hexahydrochloride.

acid radicles of linolenic, linolic and oleic acids respectively, and whose amounts are variable within small limits depending on the age of seed containing the oil. The amounts of the radicles of saturated glycerides are comparatively small, but their presence in linseed oil is of importance in connection with the sparing solubilities of their lead salts in oils and in varnish thinners.

Fahrion⁶ considers linseed oil to contain the following acids as glycerides :

	Per cent.	
Linolenic acids	38	$C_{17}H_{29}CO \cdot OH$
Linolic acid	30	$C_{17}H_{21}CO \cdot OH$
Oleic acid	15-20	$C_{17}H_{33}CO \cdot OH$
Saturated fatty acids	8.6	$C_{17}H_{35}(COOH \text{ and } C_{15}H_{31}COOH$
Unsapönifiable matter	0.6	(stearic) (palmitic)

Friend,⁷ after summarising the evidence to date, states the percentage composition of linseed oil to be as follows :⁸

	Per cent.	Per cent.
Saturated organic acids	10	10
Oleic acid	5	5
Linolic acid	48.3	59.1
Linolenic acids	32.1	21.3
Glyceryl radicle	4.6	4.6

In view of the importance of the presence of saturated glycerides, which do not dry and produce sparingly soluble soaps, a few details of their identification and estimation are advisable.

Haller,⁹ by the alcoholysis of linseed oils from various sources, separated by fractional distillation the methyl esters of stearic and palmitic acids, with traces of arachidic acid. Morrell¹⁰ found that when linseed oil is heated with lead oxide the solid which separates (drying oil bottoms), especially when the oil is thinned with turpentine or white spirit, contained stearic and palmitic acids. The yield of the lead salts was 8.2 per cent of the Calcutta oil taken, which corresponds to 6 per cent saturated acids. The composition of the mixed acids was summarised as follows : Stearic acid 64 per cent, palmitic acid 20 per cent, eutectic mixture of stearic and palmitic acids 8 per cent ; oleic acid, 4 per cent ; total, 96.4 per cent. The lead salts contained no arachidic acid ($C_{20}H_{40}O_2$).

The most important components of linseed oil are the glycerides of linolenic acid ($C_{18}H_{30}O_2$) and linolic acid ($C_{18}H_{30}O_2$). Before giving a brief account of the properties of the acids it will be advisable to describe several members of the unsaturated acid series so as to obtain some idea of the functions of doubly linked carbon atoms in the open chain arrangement on which the constitutional formulæ are based.

OLEIC ACID SERIES, $C_{18}H_{34}O_2$

Ordinary oleic acid, Δ^9 -10 octodecylenic acid ($CH_3(CH_2)_7CH=CH(CH_2)_7COOH$), with its stereoisomer elaidic acid

$\left(\begin{array}{c} \text{CH}_3(\text{CH}_2)_7 \cdot \text{CH} \\ \parallel \\ \text{COOH}(\text{CH}_2)_7\text{CH} \end{array} \right)$, are the best known members of this class.

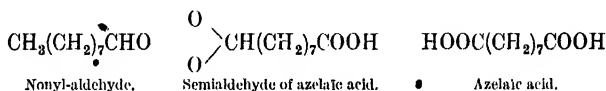
Five acids of the formula $\text{C}_{18}\text{H}_{34}\text{O}_2$ have been obtained from natural fats, and it is evident that the number of isomers will be large as the position of the double linkage is changed. Two varieties may be mentioned, viz. iso-oleic acid $(\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CH}(\text{CH}_2)_6\text{COOH})$, m.p. $44^\circ\text{--}45^\circ\text{C.}$ and petroselenic acid $(\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH})$ obtained from parsley seeds, m.p. 33°C. and yielding an elaidic acid, m.p. 54°C. No member of the oleic acid series has been synthesised, although the report of the Food Investigation Board, 1920, describes attempts that are being made to synthesise $\Delta 9\text{--}10$ octodecylenic and $\Delta 10\text{--}11$ octodecylenic acid (isoleic acid). No doubt the synthesis will be accomplished and the constitutional formulæ of the acids established; at present they rest on the results of investigations on their decomposition products. The investigations of Baruch¹¹ on the decompositions of the oxims obtained from stearolic acid, and of Harries and Erdmann and Bedford on the decomposition of the ozonides, have met with success, although the constitutional formulæ set forward have been challenged as not explaining all the properties of the acids, especially in the case of the more unsaturated members of the open-chain series.

Oleic Acid, 9, 10, or 11. Oleic Acid: $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$. —This acid is of interest to the varnish maker as a minor component of linseed oil and because of the properties of some of its metallic salts. In its pure form it is best prepared from tallow which does not contain any less saturated acids. The fat is saponified by caustic alkali and the lead salt precipitated by lead acetate and extracted with ether. The solution of lead oleate in ether is decomposed by hydrochloric acid, and after removal of the ether the oleic acid is purified by neutralising with ammonia and precipitated as the barium salt by barium chloride. Barium oleate is recrystallised from alcohol, and the acid obtained by decomposing the salt with tartaric or a mineral acid. The oleic acid thus obtained still contains solid acids, and it has been suggested that the ICl compound should be prepared and separated from the saturated acids by an organic solvent from which the purified compound can be decomposed by aniline and the pure acid obtained. Oleic acid melts at $14^\circ\text{--}16^\circ\text{C.}$ and is probably dimorphous. On distillation at the ordinary pressure it is decomposed into water, carbon dioxide, acetic acid, caprylic ($\text{C}_8\text{H}_{16}\text{O}_2$) and caproic ($\text{C}_6\text{H}_{12}\text{O}_2$) acids, sebacic acid ($\text{C}_{10}\text{H}_{18}\text{O}_4$) and hydrocarbons, but it can be distilled unchanged in superheated steam at 250°C. , which is the commercial method of obtaining oleic acid from fats. It is insoluble in water, soluble in alcohol, and on exposure to air it becomes rancid, giving cönanthaldehyde ($\text{C}_7\text{H}_{12}\text{O}$), formic, acetic, butyric and cönanthic acids ($\text{C}_7\text{H}_{14}\text{O}_2$), which are also the products of the rancidity of olive oil. Oxidation by alkaline permanganate¹² gave 60 per cent dihydroxystearic acid ($\text{C}_{17}\text{H}_{33}(\text{OH})_2\text{COOH}$), 16 per cent

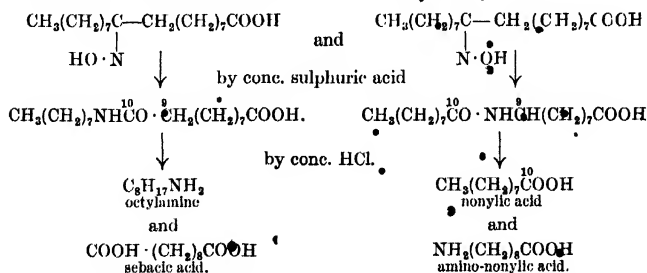
pelargonic acid ($C_9H_{18}O_2$), and 16 per cent oxalic acid. If enough alkali be present to neutralise only the oleic acid used, keto-hydroxystearic acid as well as dihydroxystearic acid is obtained.¹³

The absorption of ozone by unsaturated acids is of great importance in elucidating their structural formulæ. Harries¹⁴ and Molinari¹⁵ obtained an ozonide $CH_3-(CH_2)_7-\overset{\overset{O}{\parallel}}{CH}-CH(CH_2)_7COOH$,

which is a yellow oil easily soluble in benzol and chloroform. Harries maintains that under certain conditions perozonides ($C_{18}H_{34}O_6$ and $C_{18}H_{34}O_7$) can also be obtained. The ozonide is decomposed by water to give nonyl-aldehyde, nonylic acid, the semialdehyde of azelaic acid, and azelaic acid.



Glacial acetic acid will also cause the same decomposition, but if an alkali be present the aldehydes are oxidised to acids by the sodium peroxide formed. The ozonides are saturated substances which do not decolorise bromine, but they are oxidising agents and liberate iodine from potassium iodide. The position of the double linkage in the oleic acid molecule, demonstrated by the decomposition of the ozonide, has been confirmed in another way by Bajuch (*loc. cit.*), who transformed oleic acid into dibromostearic acid, which on treatment with alcoholic potash gave stearolic acid $CH_3(CH_2)_7C \equiv C(CH_2)_7COOH$, and on treatment with concentrated sulphuric acid gave ketostearic acid $CH_3(CH_2)_7CO-(CH_2)_7COOH$. Ketostearic acid forms with hydroxylamine two stereo-isomeric oxims, which are decomposed by sulphuric and hydrochloric acids successively according to the following scheme:—



Therefore the double linkage in the chain lies between the C, 9 and C, 10 atoms.

Just as oleic acid unites with two atoms of bromine to give dibromostearic acid, so it can be made to unite with two atoms of hydrogen to give solid stearic acid, using a nickel catalyst by the

well-known Sabatier's process or at the ordinary temperature by colloid platinum as catalyst. Oleic acid dissolves in concentrated sulphuric acid to give $C_{18}H_{35}(HSO_4)_2O_2$, which on treatment with

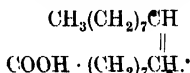
boiling water gives hydroxystearic acid $C_{17}H_{34}$ $\begin{matrix} \text{OH} \\ \text{COOH,} \end{matrix}$ together

with an anhydride of that acid.

Fusion with solid potash yields palmitic acid, as in the case of elaidic acid, which is the product of the action of nitrous acid and is the isomer of oleic acid.

The oleates of interest to the varnish maker are (1) lead oleate, m.p. 45° - 50° C., soluble in ether, but not so completely as to allow of separation from saturated acids; it is soluble in petroleum ether and does not occur in varnish bottoms. Lead oleate may also be used as a drying catalyst in oil varnishes. (2) Aluminium oleate is gelatinous, sparingly soluble in ether, petroleum ether and benzene, and is used as an oil thickener. It is insoluble in alcohol. (3) Barium oleate is insoluble in water, but soluble in a mixture of benzol and alcohol containing 5 per cent of 95 per cent alcohol, from which it can be crystallised on cooling the solution.¹⁶

Elaidic Acid.—The action of nitrous acid on oleic acid yields a stereoisomeric crystalline modification of the formula—



Elaidic acid crystallises in plates melting at 44.5° C. and can be distilled under reduced pressure (b.p. 234° C. 15 mm.). In chemical properties it closely resembles oleic acid; on reduction it yields stearic acid; on oxidation the products are dihydroxystearic acid $C_{18}H_{34}O_2(OH)_2$ (m.p. 99° C.) 33 per cent, pelargonic acid, $[C_9H_{18}O_2$ nonylic acid] 13.44 per cent, azelaic acid 26 per cent, and oxalic acid 15.20 per cent. The action of fused caustic potash and of concentrated sulphuric acid are similar to those observed with oleic acid. The barium, lead, and silver salts are sparingly soluble in ether.

The action of nitrous acid on unsaturated fatty open-chain acids is restricted to the less unsaturated members, and acids of the linolic and linolenic series do not yield modifications.

LINOLIC ACID SERIES, $C_{18}H_{32}O_2$

There are a number of acids having the formula $C_{18}H_{32}O_2$ which contain two doubly linked pairs of carbon atoms and one acid containing a triply linked pair of carbon atoms (tariric acid, $CH_3(CH_2)_{10}C \equiv C(CH_2)_4COOH$).¹⁷ The two most important members

* Tariric acid is obtained from the oil of the seeds of the Guatemalan "Tariri". It absorbs four atoms of bromine and yields stearic acid on reduction.

are linolic acid and elæostearic acid, which occur as glycerides in certain oil seeds. Ricinoleic ($C_{18}H_{34}O_2$) and ricinelaïdic acids are transformable into solid modifications of an acid $C_{18}H_{32}O_2$.¹⁸

Linolic Acids.—The glyceride of linolic acid occurs in considerable proportion in drying and semi-drying oils, and is most readily obtained from poppy seed, Soya bean, maize, cotton seed and sesame oils by brominating the mixed fatty acids, purifying the tetrabromide by recrystallising from petroleum ether and reducing it with zinc and hydrochloric acid in methyl alcohol solution. The methyl ester of linolic acid is saponified in the cold with alcoholic caustic potash and the acid liberated by dilute hydrochloric acid. The glyceride of linolic acid is present also in a large number of non-drying oils and fats; cf. lard, horse fat, etc.

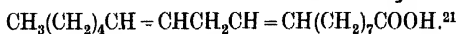
Linolic acid is a liquid with a specific gravity 0.9026 at 18° C., b.p. 229°-230° C. at 16 mm. It is soluble in alcohol and in ether.

With nitrous acid it yields no solid isomeride. Linolic acid absorbs oxygen as a thin film and is converted within a few days into a solid resinous substance, passing to a neutral body (a linoxyn), which is insoluble in ether. The tetrabromide, m.p. 114°-115° C., is obtained in two forms, one soluble in petroleum ether and the other insoluble in that liquid. Rollett¹⁹ obtained a 50 per cent yield of solid tetrabromide and 50 per cent of the fluid variety, which furnished on reduction an acid yielding a crystalline tetrabromide (m.p. 113°-114° C.), but only to the extent of 26 per cent of the calculated yield. He concluded that two isomeric bromo-acids were formed in the bromination. On the other hand, Bedford²⁰ maintained the existence of two isomeric linolic acids.

Oxidation by potassium permanganate yields sativic acid (tetrahydroxystearic acid, $C_{18}H_{36}O_6$).

Rollett (*loc. cit.*) obtained a 40 per cent yield of a tetrahydroxy-acid (m.p. 155° C.) which on boiling with benzene and recrystallisation from alcohol gave an acid (m.p. 171°-173° C.). He maintained that two isomeric hydroxy-acids are produced in the oxidation.

The constitutional formula is put forward as



Linolic acid is easily reduced by hydrogen and a nickel catalyst to stearic acid. The calcium, barium, zinc, copper, and lead salts are soluble in ether; barium linoleate is soluble in benzene and light petroleum (cf. barium oleate). The methyl ester is a liquid (b.p. 211°-212° C. at 16 mm., s.g. 18° C., 0.886), and is obtained from the tetrabromide by reduction with zinc and hydrochloric acid in methyl alcohol solution.

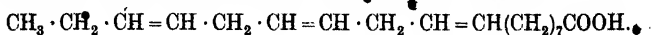
Elæostearic Acid, $CH_3(CH_2)_2CH=CH(CH_2)_2CH=CH(CH_2)_7COOH$, does not occur in linseed oil, but it can be obtained in two stereoisomeric forms (m.p. 48° and 71° C.) from tung oil. Both modifications give a tetrabromo acid (m.p. 114°-115° C.) which is not identical with the tetrabromo acid from linolic acid.²²

LINOLENIC ACID SERIES, $C_{17}H_{32}COOH$

Linolenic Acid.—This acid was first prepared by Hazura²³ from the crystalline hexabromide (m.p. 177° C.) obtained from linseed oil. By reduction of the hexabromide with zinc and hydrochloric acid Hehner and Mitchell²⁴ obtained a nearly colourless oil (s.g. 0.9228, 15.5° C.). It may also be prepared by boiling the hexabromide with zinc and alcohol, or by reduction of the ethyl ester of hexabromolinolenic acid and saponification of the resulting ethyl ester. The acid boils at 157° - 158° C. (0.001 mm.) (Bedford) without decomposition, or at 230° - 232° C. (17 mm.).²⁵

As to the existence of α - and β -linolenic acids the evidence is not conclusive, although there is a tendency to accept their presence in linseed oil. The physical properties of the two acids are not sufficiently differentiated as in the case of oleic and elaidic acids. Controversy between Erdmann, Bedford, and Rollett is due to the fact that linolenic acid from linseed oil yields only 25 per cent of hexabromo acid on rebromination and 77 per cent of a tetrabromide of β -linolenic acid. Rollett maintains that the tetrabromide of β -linolenic acid is unsaturated and yields a hexabromide on further treatment with bromine. On bromination of linolenic acid four bromo-addition products could be obtained, and if one only be crystalline then the 25 per cent yield is accounted for. Erdmann, Bedford, and Raspe²⁶ state that two ozonides are obtainable from linolenic acid, produced by the reduction of the crystalline hexabromide, which are differentiated by their velocity of decomposition with water.

Linolenic acid is a colourless liquid soluble in ten parts of light petroleum, absorbs oxygen readily, and manifests a tendency to polymerisation, although definite proof of this is not forthcoming. The methyl and ethyl esters boil at 207° C. (14 mm.) and 132° C. (0.001 mm.) respectively. The melting-point of linolenic acid hexabromide is 177° - 182° C. (185° C., Coffey), and the melting-point of its ethyl ester is 151° C. Iodine and bromine trichlorides react to give trichlorotriiodo, $C_{18}H_{30}O_2I_3Cl_3$, and tribromotriiodostearic acids, $C_{18}H_{30}O_2I_3Br_3$ respectively (m.p. 146° C. and m.p. 124° - 126° C.). Combination with hydrogen to give stearic acid is brought about by a nickel catalyst to give a quantitative yield of stearic acid (Erdmann and Bedford). The ozonides on decomposition with water give propionic aldehyde, malonic acid, and the aldehydes of malonic and azelaic acids, and it is on these decomposition products that the constitutional formula of linolenic acid is based.²⁷



By oxidation with potassium permanganate Hazura obtained two hexahydrostearic acids, linusic and isolinusic, which fact does not support the existence of the α - and β -acids, because either form of the so-called α - and β -linolenic acids yields linusic and isolinusic acids on oxidation (Rollett).

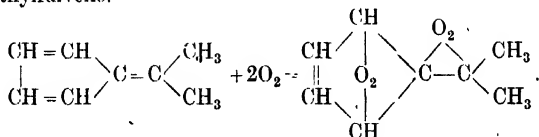
The basic zinc salt $[\text{C}_{18}\text{H}_{33}\text{O}_2]_2\text{Zn} + \frac{1}{2}\text{ZnO}$ (m.p. $72^\circ\text{--}73^\circ\text{C.}$) used by Erdmann²⁸ for the preparation of a pure acid from linseed oil acids by fractional crystallisation from alcohol has been found by Coffey²⁹ to be unsatisfactory, as it does not effect separation from linolic acid.

The lead and barium salts of linolenic acid are easily soluble in ether. Like linolic acid, no isomeride is obtained on treatment with nitrous acid.

OXIDATION OF LINSEED OIL

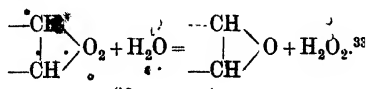
From the general properties as indicated by the constitutional formulæ of the component glycerides it is presumed that oxidation will proceed in stages, whereby a molecule of oxygen becomes attached where there is a double linkage. The absorption is gradual, and depends on the conditions of temperature and of

illumination. Peroxides of the type $\begin{array}{c} \text{O} - \text{O} \\ | \quad | \\ \text{C} - \text{C} \\ | \quad | \end{array}$ are formed primarily from linolenic and linolic acids, so that in linoleum there are glycerides of diperoxylinolenic and peroxylinolic acids. A similar addition of oxygen may be illustrated in the oxidation of dimethylfulvene.³⁰



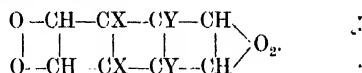
Which of the double linkages absorbs oxygen first is not definitely known. In China wood oil the double linkage nearest the COOH group is probable, although Ingle³¹ states that the doubly linked carbon atoms in proximity to the COOH groups may be prevented from absorbing halogens from a strongly acid solution.

A complete examination of the oxidation stages of drying oils is much wanted. If the glyceride of β -elæostearic acid³² were made the starting-point it would be possible to follow the different stages satisfactorily. The glyceride is a monomolecular crystalline substance, which is oxidised with great rapidity. On exposure to air it yielded a substance, $(\text{C}_{18}\text{H}_{31}\text{O}_4, \text{C}_2)_3\text{C}_3\text{H}_5$, which could be heated to 230°C. without melting. It is a peroxide, yielding hydrogen peroxide when boiled with water with the formation of a yellow substance of spongy texture, and liberating iodine from potassium iodide and dilute acetic acid. The action of water may be represented by the scheme :

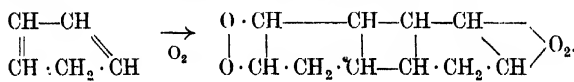


The oxidation of drying oils in air is a case of autoxidation; a term which is applied to processes of combustion in oxygen or air which take place at the ordinary temperature and proceed with slow but measurable velocity under these conditions. Well-known cases are found in the combustion of phosphorus, in the oxidation of certain liquids, *e.g.* benzaldehyde, turpentine, in the conversion of sulphites of sodium and zinc into sulphates, and in the corrosion or rusting of many metals, *e.g.* zinc and iron.³⁴ The changes occurring subsequent to the formation of peroxides may be numerous, and have been the subject of discussion by many investigators. In addition to oxidation, polymerisation may occur.

Fahrian³⁵ suggests a linkage up of the molecules through the remaining unsaturated carbon atoms.



Ingle³⁶ considers that polymerisation during oxidation rests on insufficient evidence. The recent work by Stobbe and Dunhaupt³⁷ on cyclopentadiene, which is transformed on oxidation into diperoxide dimeride, supports the polymerisation view.



Such polymerisation is slower than the oxidation. The writer has shown in the case of oxidised China wood oil that polymerisation subsequent to oxidation actually occurs.³⁸

Wolff³⁹ maintains that in the case of oil varnishes on exposure to light of short wave-length oxidation and polymerisation proceed at nearly equal rates, whereas in light of long wave-lengths polymerisation is retarded more than oxidation, with the result that inequality of the outer and inner layers occurs with the production of rivelled films. Polymerisation is of great importance in the consideration of durability and water-resisting power of oil films. The table on following page shows the percentage of ether-insoluble linoxyn obtained from several varieties of drying oils. It is evident that the linoxyn produced from polymerised oil is greater in amount and the film is more water-resisting than that obtained from ordinary linseed oil. There is evidence of differences between the action of lead and manganese as driers which will be referred to under that section.

H. Wolff⁴⁰ has found that the interior and exterior layers of a compact block, formed by soaking thin tissue paper in linseed oil and pressing together and allowing to dry, when examined show nearly equal iodine values, although the proportion of oxidised fatty acids in the outer layers was considerably higher. The phenomenon is probably due to rapid oxidation of the oil on the outer layers simultaneously with strong polymerisation in the inner layers. More prolonged drying diminishes the difference.

TABLE I
WATER-ABSORPTION OF DRYING OIL FILMS AFTER TREATMENT WITH
LIGHT PETROLEUM AND METHYLATED ETHER

	Time of Air Drying.	Treatment with Light Petroleum. 3 days.	Treatment with Light Petroleum. 6 days.	34 days in Methylated Ether.	Per cent. Linoxyn.	Water-Immersion. Per cent gain.			
						1 day.	2 days.	4 days.	8 days.
Linseed oil Pb and Mn present	160 days	% loss. 3.8	unchanged	% loss. 35.3	60.9	23.8 film white	29.6 film white	33.5 film white	52.9 film white
Linseed oil Pb and Mn present	30 days	60.5 62.4	39.5 37.6	..	3 days 21.6 32.5 } film white		
Lithographic oil Pb and Mn present	30 days	40.7	59.3	..	3.4 film white		
Lithographic oil Mn present	30 days	46.4	53.5	..	15.2 film milky		
Linseed oil Pb and Mn present	12 hrs.	68.8	31.2	18.0 film cloudy	5 days 23 film white		

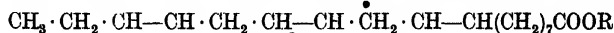
between the layers. There is evidence in the specific action of certain metals in the drying process which favours promotion of a similar polymerising action or of changes indicated by Rochs in his formulæ for the oxidation products of drying oils. Stransky⁴¹ puts forward the oxidation process as occurring in two stages: (1) oxidation; (2) coagulation of oxidised oil from the fluid to the solid form. Coagulation and polymerisation are related, and to produce the complete solidification of the film promoters and catalysts are essential. This view will be referred to later in the discussion on the action of metallic driers.

It has been suggested that the primary peroxides may react with molecules of unoxidised oil to give oxides $AO_2 + A = 2AO$ or $AO_2 + B = AO + BO$ (where B is another drying oil; e.g. the glyceride of linolic acid). Fokin⁴² considers that the primary product of

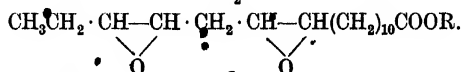


the oxidation is an oxide $\begin{array}{c} \diagup \quad \diagdown \\ O \end{array}$, whereas Orloff⁴³ suggests

that linolenic and linolic glycerides yield on oxidation respectively

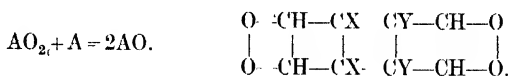


and



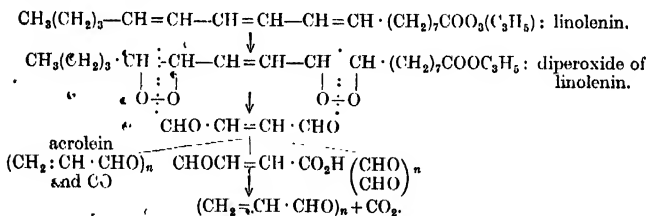
These formulæ do not account for the presence of unsaturated carbon atoms in linoxyn, since glycerides of diperoxylinolenic acid

are stated to be present in linoleum.⁴⁴ The triperoxylinolic glyceride has not been identified,⁴⁵ although it may represent the autocatalyst formed during the oxidation of linseed oil in the absence of catalyst (driers), and it would appear as if the diperoxylinolenic acid glyceride were the maximum grade of oxidation which can be identified among the oxidation products of linseed oil.* The evidence of the formation of peroxides is generally admitted, as well as their presence in linoxyn, which must be considered as a complex of oxidised mixed glycerides. With regard to the subsequent changes in linoxyn there is no consensus of agreement. The possibilities are very many, comprising acids, aldehyde acids, substances with a definite acetyl value and volatile products.⁴⁶



The last change is very probable, and is shown markedly in the oxidation of China wood oil. It probably occurs side by side with the formation of an oxide of the type AO. Which of the two changes occurs depends on the conditions of the oxidation and on the nature of the promoter (drier).

Salway⁴⁷ suggests that linoxyn consists of olein and polymerised aldehydes derived from the decomposition of oxidised linolin and linolenin (glyceride of linolenic acid), and presumes for linolenic acid the constitutional formula of a derivative of hexatriene to account for the presence of acrolein and oxides of carbon among the volatile oxidation products of the oil.



De Waele (*loc. cit.*) considers that linoxyn consists of peroxides with polymerised aldehyde-glycerides.

The constitutional formula of linolenin rests on the work of Raspe and Erdmann, and Salway's suggestion requires rearrangement of the double linkages during the process of oxidation. The writer favours the oxide-formation-with-polymerisation proceeding simultaneously with the decomposition of the peroxides into simpler substances of an acidic and aldehyde character.⁴⁸

In order to obtain more information on the secondary changes it is advisable to consider the change in weight when linseed

* See page 33.

oil absorbs oxygen. If a layer of linseed oil, 0.1–0.2 gram per 100 sq. cms., be spread on glass, the maximum gain in weight at the ordinary temperature is 19 per cent of the weight of the oil taken. Lippert⁴⁹ states that with a normal linseed oil the film must be dry at the attainment of its maximum weight. If the film be wrinkled or if drop-like aggregates be visible, impurities are present, due to adulteration with rosin or foreign seed. If the experiment be carried out in an atmosphere of dry air, the time for attainment of the maximum weight will be reduced. The rate of absorption depends on the temperature, atmospheric conditions, and on the presence of catalysts. It is slower in a moist atmosphere than in a dry. The absorption is accompanied by a decomposition due to the degradation of the peroxides previously referred to. The decomposition products comprise volatile substances; e.g. carbon dioxide, water, formic and acetic acids, acrylic acid,⁵⁰ $C_3H_4O_2$, acrolein, C_3H_4O , and butyric acid.⁵¹ Carbon monoxide has been stated to be present by some investigators.⁵² Klein⁵³ criticises the experimental work, although King⁵⁴ maintains its presence. It may be considered that if carbon monoxide be formed it is only in quantities insufficient to have any toxic action, whereas the aldehyde vapours are bactericidal. Experience at linoleum works in the oxidising sheds has shown that the vapours evolved during the oxidation of linseed oil have no toxic effects on the workmen.⁵⁵

Moisture and soluble ferments cause hydrolysis, and the free fatty acids produced are oxidised in the air, yielding decomposition products, some acidic, some aldehydic (cf. the odour of valerianic aldehyde from China wood oil). In rancid cotton oil 0.6 per cent free and 9.8 per cent combined azelaic acid have been found.⁵⁶ Rancidity of oils is also the result of an oxidation process with the production of volatile aldehyde substances.

The quantitative relations between increase in weight of film, volume of oxygen absorbed and time, as well as the influence of moisture, have been investigated by a number of workers,⁵⁷ for whose results see Friend (*Chemistry of Linseed Oil*, p. 46). The relationships are shown in Fig. 1.

According to Lippert, at the point C the oil is dry, and setting occurs between B and C. The position of C, as to gain in weight, varies from 13 per cent to 25.6 per cent (Wilson and Heaven show 18 per cent). The point C represents the point of equilibrium at which the gain in weight is approximately equal to the loss in weight due to escaping vapours and gases. Any factor assisting or retarding the removal of the oxidation products will proportionally lower or raise the position of the point C.⁵⁸ The graph in Fig. 2 shows that the weight of oxygen absorbed is much greater than the gain in weight on oxidation.

Genthe (*loc. cit.*) found that linseed oil could absorb 22.6 per cent of oxygen, in Uviol light 25.8 per cent, whilst at 95° C. 26.8 per cent (in air) and 34.7 per cent (in oxygen).

The following Table shows the changes in weight, density, and

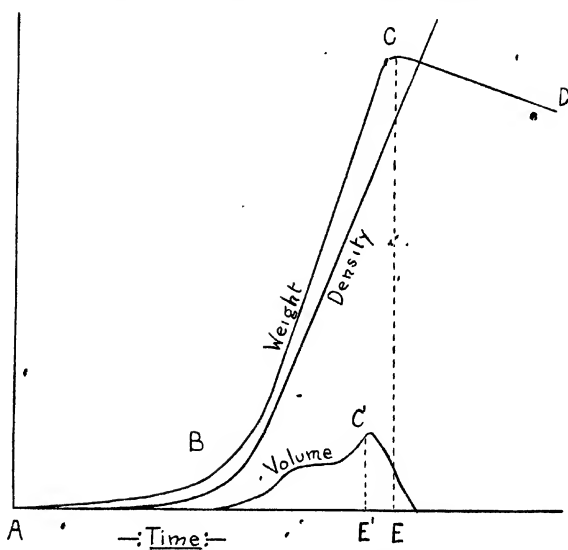


FIG. 1.—Behaviour of linseed oil during drying. (Friend.)

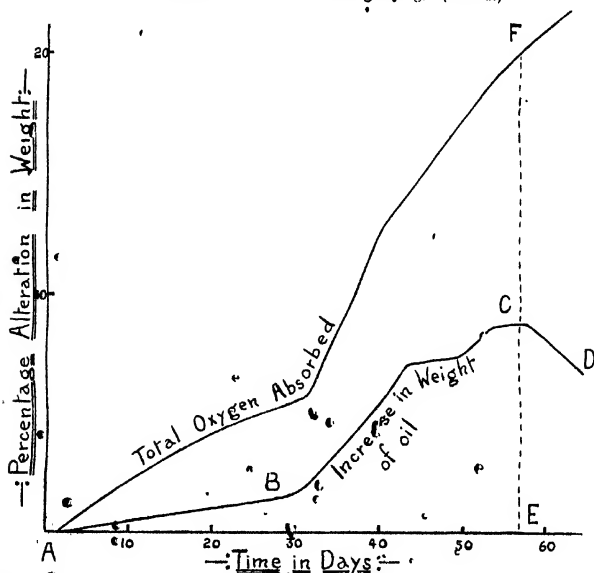


FIG. 2.—The alteration in weight during the setting of linseed oil and the total amount of oxygen absorbed. (Friend.)

volume, when thin films of linseed oil are spread on glass and allowed to oxidise at the 15° C.:

	Per cent Increase in Weight.	Density at 0°.	Density at 10° C.	Coefficient of Expansion, 0°-15° C.	Per cent Increase in Volume at 15° C.
Raw oil	0.94208	0.93179	0.00074	..
Raw oil liquid	2.08	0.95906	0.94850	0.00074	0.28
Raw oil liquid	5.83	0.98736	0.97696	0.00074	0.87
Thick frothy liquid . .	9.66	1.01161	1.00123	0.0069	2.06
Tacky	14.14	..	1.0424	..	2.0
Just set	17.34	..	1.0582	..	3.3
Solid linoxyn	17.90	..	1.0656	..	3.1
„ „ at max. weight	18.57	..	1.0902	..	1.4
Three months old . . .	10.3	..	1.1054	..	7.0

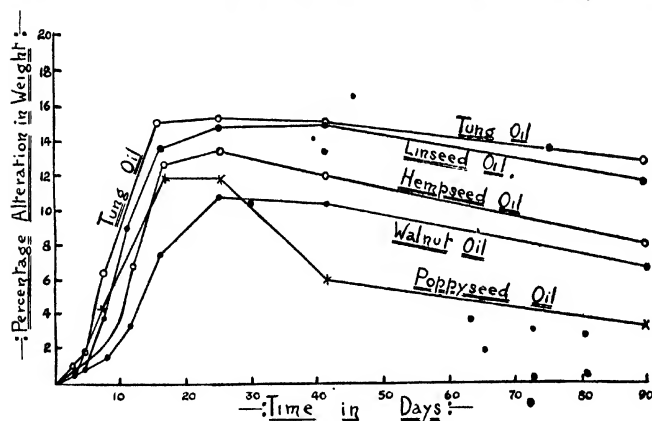


FIG. 3.—Percentage alteration in weight of oils at room temperature. (Friend.)

Under the particular conditions of the experiments the raw oil on setting at 15° C. expanded by 3.3 per cent and then slowly contracted. The maximum apparent increase in weight was 18.57 per cent, but the increase in volume reached its maximum at the setting point. Whether any sudden contraction or expansion occurs at the time of setting is unknown.

Sabin⁵⁹ found that a film of raw oil gave linoxyn of density 1.098 (assuming the density of the original oil to have been 0.9332) with a total gain in weight of 2 per cent, so that the shrinkage must have been 13.4 per cent.

Any factor assisting in the decomposition of the oil lowers the maximum of the increase in weight and reduces the expansion.

Sabin (*loc. cit.*) and Gardner⁶⁰ found that linseed oil, when

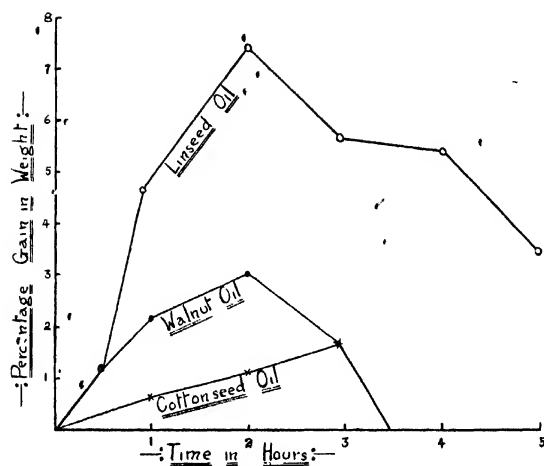


FIG. 4.—Percentage alteration in weight of oils at 100° C. (Friend.)

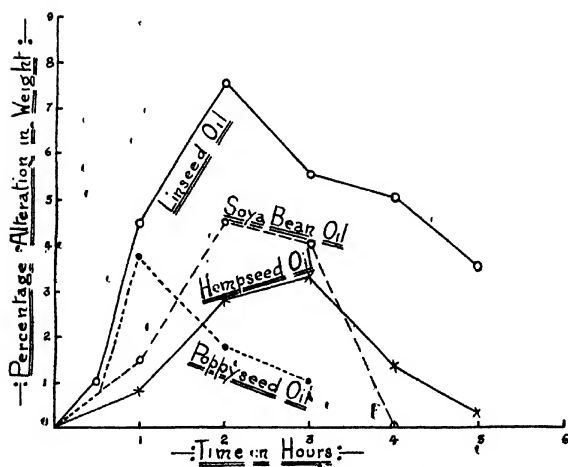


FIG. 5.—Percentage alteration in weight of oils at 100° C (Friend.)

mixed with chemically inert powders such as barytes and silica, exhibits a smaller increase in weight on setting, so that the powders assist catalytically in the decomposition of the peroxide compounds.

It is advisable to refer again to the view as to the fate of the peroxides. The transformation of $AO_2 + A$ into $2AO$ proceeds

simultaneously with $\begin{matrix} -X \\ -X \end{matrix} \rangle O_2 \rightarrow \begin{matrix} \cdot XO \\ \cdot XO \end{matrix}$, where the molecule is

disrupted with the formation of volatile products, loss in weight, and loss in body and lustre. It will be evident how such a factor as polymerisation or the use of "stand oil" will retard the loss in weight and loss of lustre, and how certain driers will favour the course of the change in one of the two directions. It would be of interest if more figures were available for the changes in weight and density when polymerised oils (in the presence of a small quantity of catalyst) are exposed until the setting and drying points are reached.⁴³

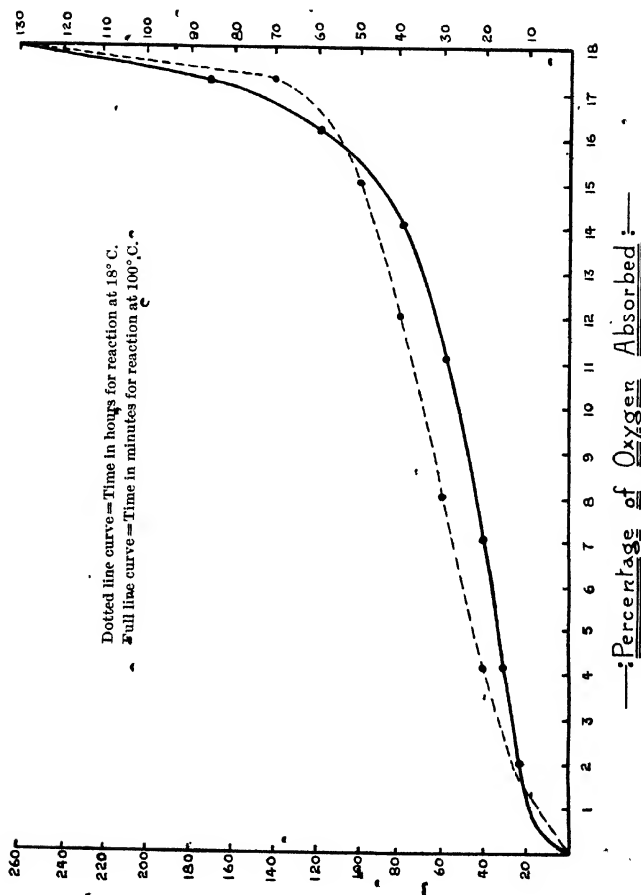
Fig. 3 shows the percentage gain in weight (apparent) of drying oils at room temperature, and Figs. 4, 5, and 6 show the influence of temperature on the percentage gain in weight.

Fokin⁶¹ found that the rate of setting of linseed oil followed Spring's rule in that it was doubled for every 10° C. rise in temperature. Moisture retards the time of setting.

INFLUENCE OF MOISTURE ON THE OXIDATION OF LINSEED OIL

The influence of moisture on the setting of oils is of importance, and will be referred to again under the drying of varnishes.

Gardner⁶² has investigated the changes in the weight of oil films, containing 0.2 per cent metallic oxide as catalyst, exposed to moist air and to dried air in a special apparatus. The results show that in every case there is a great increase in weight during the first twenty-four or forty-eight hours. The films dried in moist air almost invariably showed a gain in twenty-four hours which was equal to that shown by the same films in dry air in forty-eight hours; this gain was followed by a decrease, in some cases amounting to more than the original gain. Still later, and in the majority of cases, the weight increased again, and a second maximum was reached before the oils settled down to constant weight. The second maximum was particularly noticeable in those cases in which drying took place in a humid atmosphere, it being often greater than the first maximum. In dry air the second rise is usually slight and sometimes entirely lacking. The final hardening of the film is reached more quickly and directly in dry air than in an atmosphere saturated with moisture. In the presence of moisture there is a second rise in the weight time curve. The first decrease in weight is due to the decomposition of peroxides and the escape of volatile products resulting therefrom. The second rise in the curve is due to a reaction of the glycerides and water (see Figs. 7 and 8).



The water taken up in the secondary period is chemically combined, since it is not given up when exposed to dry air. The second decrease is held to be accounted for by the decomposition of glycerol into volatile decomposition products.

The writer considers that under ordinary conditions oil films absorb water and that this absorption proceeds during the setting and beyond, diminishing as the linoxyn increases during the oxidation.

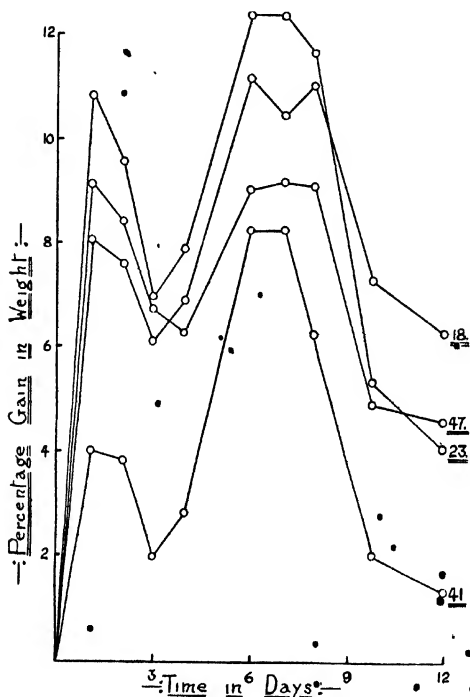


FIG. 7.—Linoleate driers (moist cabinet). No. 18, Al linoleate; No. 23, Zn linoleate; No. 41, Co linoleate; No. 47, Pb linoleate.

The second decrease may be accounted for by the gradual decomposition of peroxides according to the schemes already referred to.

De Waele⁶³ gives curves representing results obtained by plotting variations in weight shown by variously treated linseed oils on exposure to air, the atmospheric conditions being simultaneously plotted on the graph (Fig. 9).

It will be noticed that the two series of observations, viz. in light and in darkness, although agreeing in the direction of the path of the curve followed by the individual oils examined, differ very

materially. A fairly close connection exists between the inverse of the pressure of the water vapour and the light conditions, whilst the darkness conditions follow more closely the relative humidity readings. The coincidence of the paths followed by the different oils occurs after the completion of the first induction period. The relative stability of polymerised oil is shown by the steady upward tendency and closeness of the ordinates at the 53rd and 133rd day

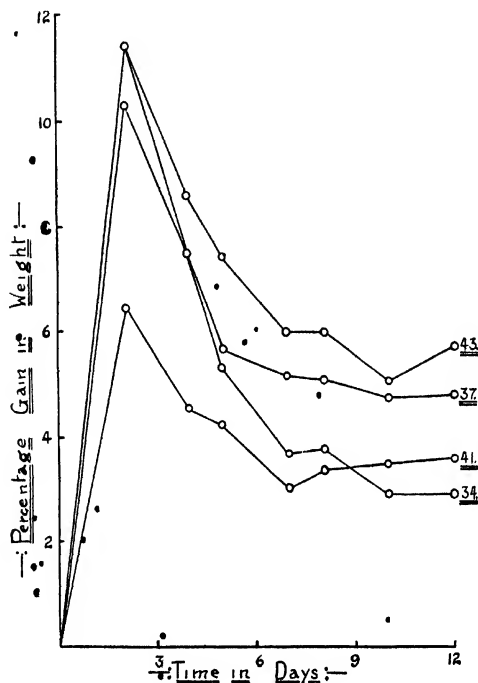


FIG. 8.—Linoleate driers (dry cabinet). No. 34, Al linoleate; No. 37, Zn linoleate; No. 41, Co linoleate; No. 43, Pb linoleate.

periods. The conclusions drawn by the author from the above curves that the periodic variations in weight are caused by two factors composing the atmospheric conditions: (1) the decomposition of the primarily formed peroxides is initiated by moisture, and (2) equilibrium conditions, *i.e.* decomposition *v.* back pressure, are attained by interpretation of the latter as pressure of water vapour.

The retardation of oxygen absorption of linseed oil in the presence of moisture is also described by Bories and Genthe (*loc. cit.*)

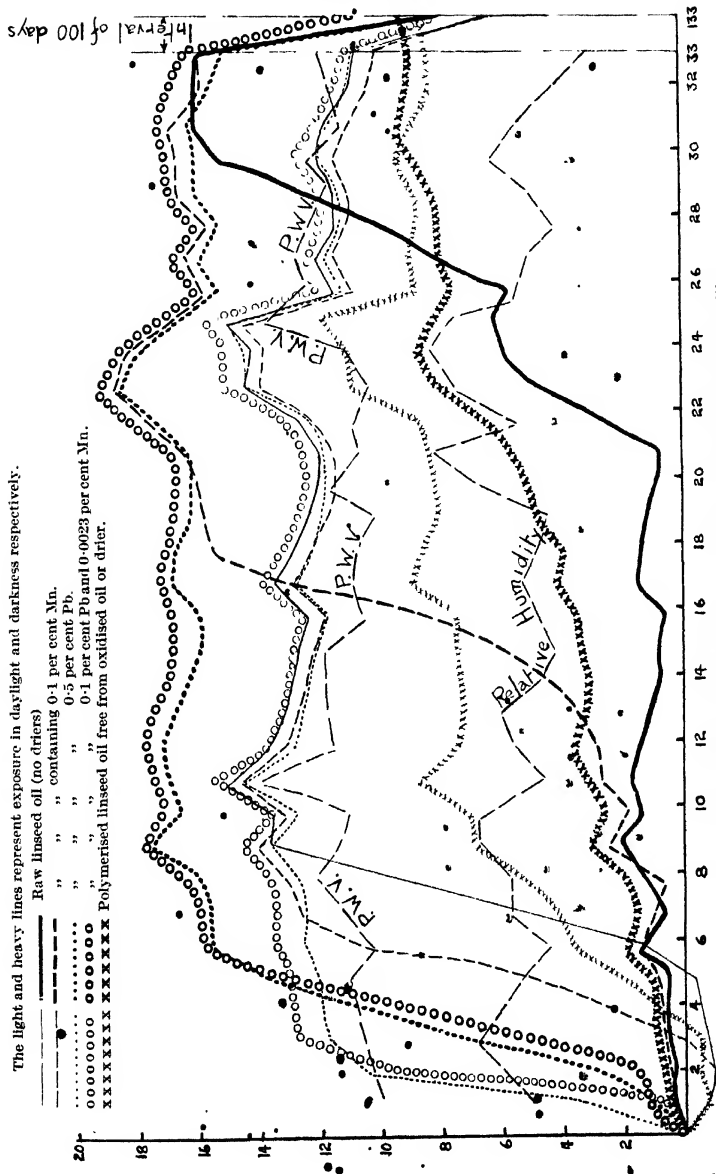


Fig. 9.—Change in weight of linseed oils under different atmospheric and light conditions.

The effect of stoving a linseed oil film at 100° C. is to increase the water-resisting power by increasing the amount of linoxyn and by acceleration of polymerisation during the drying. Friend has found that a film of linseed oil dried at 15° C. absorbed five times as much moisture as a similar film previously stoved at 100° C. He states that the painting of wrought iron while it is hot gives a much more effective protection.⁶⁴

INFLUENCE OF LIGHT ON THE OXIDATION OF LINSEED OIL

Genthe⁶⁵ showed that the absorption of oxygen by a linseed oil film was greatly accelerated by exposure to ultra-violet light.

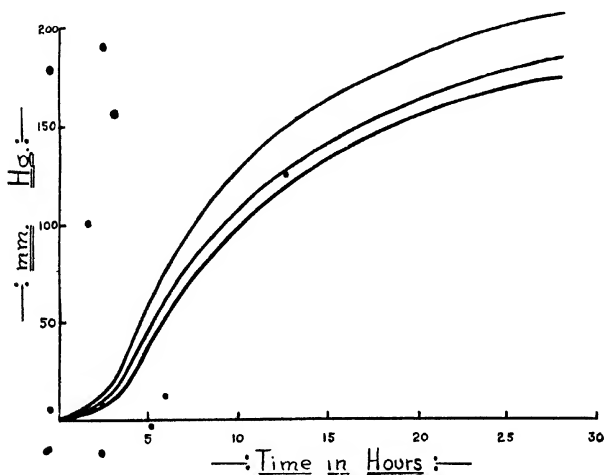


FIG. 10.—Linseed oil in light from mercury lamp.

In the dark the oxygen absorption was observed on the 20th day and the maximum was reached on the 50th day.)

The curves in Figs. 10 and 11 show the relationships between time and decrease in volume when oxygen is absorbed by linseed oil under different conditions of illumination. The results indicate that the accumulation of oxidation products in the system does not interfere with the general course of the reaction.

The form of the curves is in keeping with an autocatalytic reaction (Ostwald), and can be expressed by the equation

$$\frac{dx}{dt} = K(m+x)(a-x),$$

where a = total volume of absorbed oxygen; x = volume absorbed at t (days); m is a constant, proportional to the concentration

of the catalyst ; or if m be negligible, then the equation assumes the simple form

$$\frac{dx}{dt} = Kx(a - x).$$

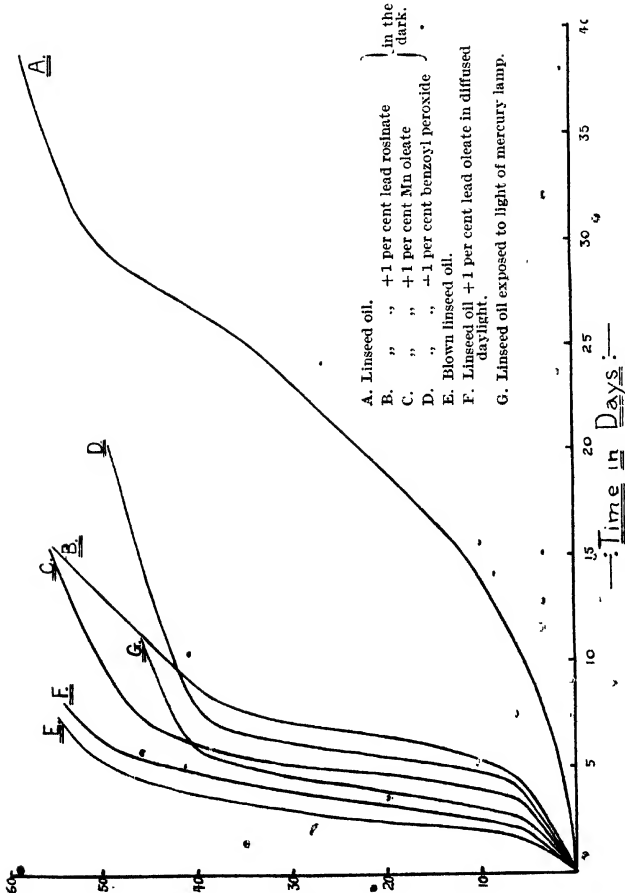


FIG. 11.—Reduction in volume of oxygen.

From the writer's own experience of long exposure of varnishes to the action of light from a mercury vapour lamp (three hundred hours), it is quite evident that there is a marked difference in the

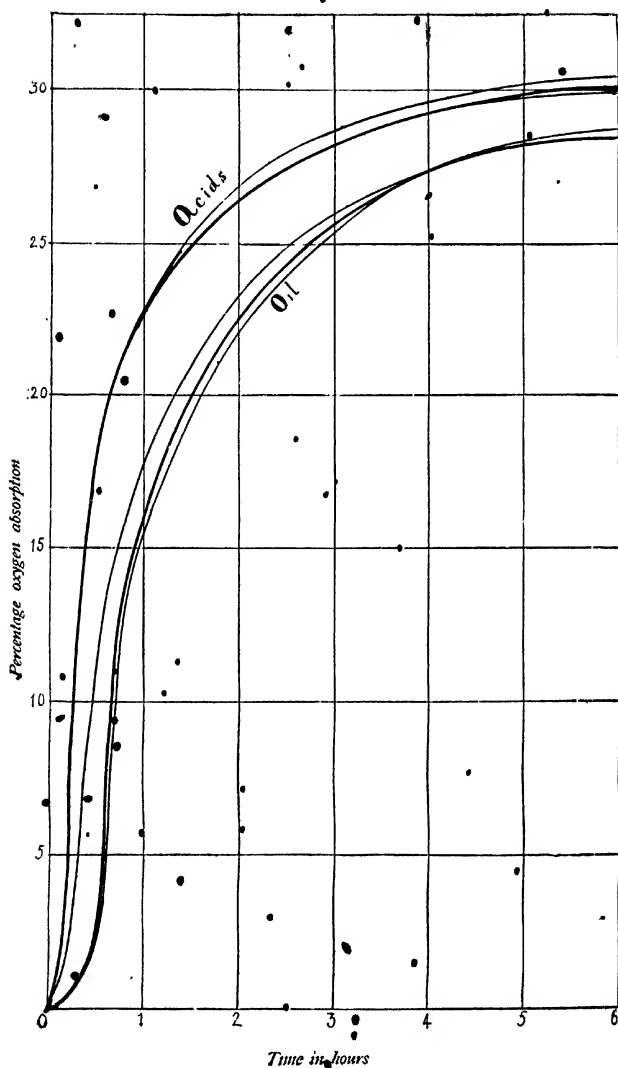


FIG. 11A.—Oxidation curves for linseed oil and linseed oil acids.

diminution of lustre of the coatings containing different amounts of polymerised oil. The coatings containing small quantities of the polymerised oil become poor and develop fine cracks, whilst the films containing larger amount of thickened oil retain their lustre to a very considerable extent without the appearance of fine cracks. It must be mentioned that the coatings were subject to alternate illumination at 140° F. and exposure to atmospheric weathering over a period which extended for three months.

Summarising the great variety of investigations on the oxidation of linseed oil, it may be concluded that the peroxide formed is not a permanent substance but gives rise to a variety of products; e.g. polymerisation substances, monoxides, and decomposition products, volatile and non-volatile. It is also evident that it is highly desirable to reduce the decomposition products as much as

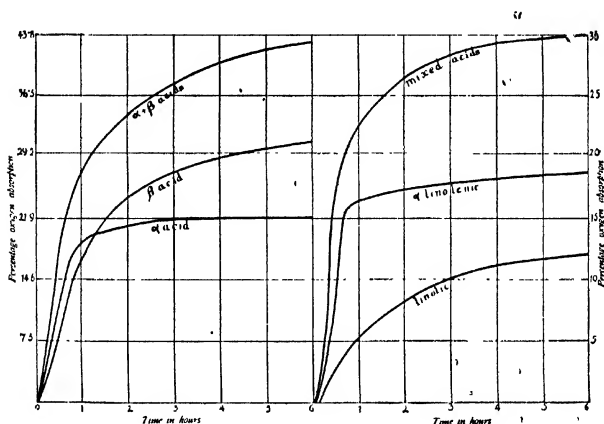


FIG. 11B.—Oxidation curves for α and β linolenic and linolic acids.

possible and to favour the polymerisation monoxide or dioxide products. It has been shown how this may be partially attained by previous thickening of the oil and by blending with another drying oil. The prevention of water absorption and loss of lustre of films are problems of the greatest importance to the varnish maker. It has already been mentioned how the nature of the catalyst may play a part not only in the quality of the oxidised film, but also in the acceleration of the drying and hardening process.

In spite of the work done on China wood oil, it is surprising how little information is available following on the lines of investigation of the theory of the oxidation of linseed oil.

In addition to the chemical changes which occur during the oxidation of linseed oil it must be remembered that linseed oil, especially thickened linseed oil, shows colloid properties on trans-

formation into linoxyn, which is a complex of oxidised and unoxidised mixed glycerides.) Changes in the dispersion of the components must be considered, and the influence of varnish solvents and varnish driers must not be neglected in that connection.

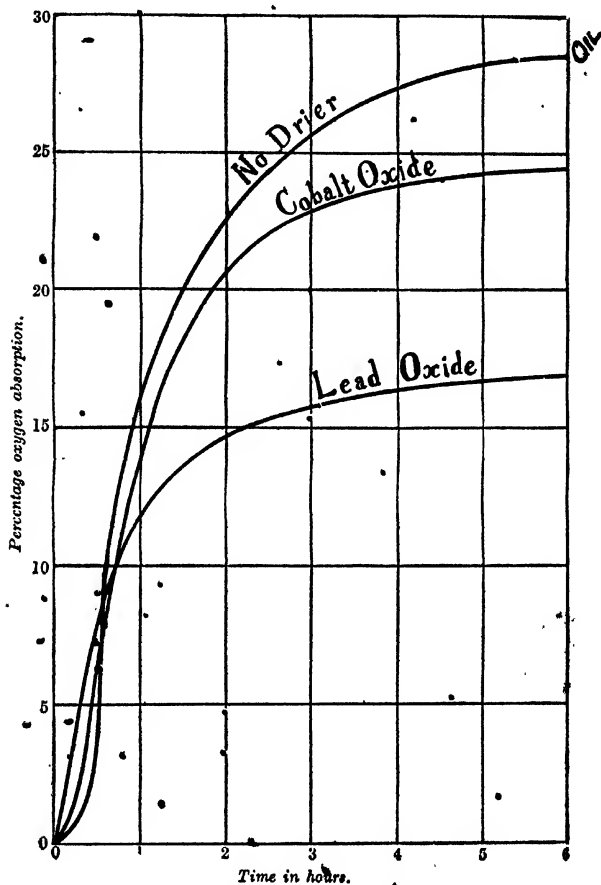


FIG. 11C.—Oxidation curves for linseed oil with and without a drier.

(Olsen and Ratner⁶⁶ state that linseed oil, after an exposure of seventy-four days to a current of pure air at the rate of 15 litres per day, absorbs 37.8 per cent oxygen, of which 18.05 per cent is permanently fixed. During the period of exposure the oil lost

1.8 per cent of its original carbon and 14.73 per cent of its original hydrogen-content.)

Coffey⁶⁵ has found that linseed oil or its fatty acids without driers gives, on oxidation at 100° C., 5.4 to 5.6 per cent of carbon dioxide, and for each molecule of oxidised linolenin or linolenic acid a molecule of carbon dioxide and a molecule of a volatile carboxylic acid (acetic) are produced. He considers that a molecule of linolenic acid reacts with 9 atoms of oxygen, of which 3 atoms form volatile products. Linolic acid gives only traces of volatile products (Figs. 11A, 11B, and 11C).

S. Coffey⁶⁷ is of the opinion that in the oxidation of linseed oil triperoxylinolenic acid and diperoxylinolenic are both formed. From the data obtained in the oxidation of linolenic and linolic acids, and from the known iodine values of the acids, the calculated composition of linseed oil agrees closely with that put forward by Friend (*Chemistry of Linseed Oil*, p. 56).

The theory of driers and the catalytic oxidation of oils will form the subject of the next chapter.

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CHAPTER II

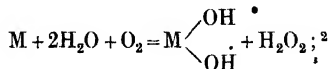
CATALYTIC OXIDATION OF OILS BY DRIERS

THE slow oxidation of linseed oil as shown in Genthe's and in Olsen and Ratner's experiments accentuates the importance of the acceleration of this oxidation by catalysts. The sinuous form of the curve expressing the relationship between amounts of oxygen absorbed and time is characteristic of an autocatalytic change¹ and can be expressed by the Ostwald equation for the introduction of an autocatalyst:

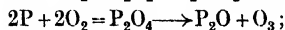
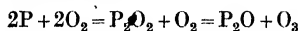
$$\frac{dx}{dt} = K(a - x)(b + x),$$

where a is the initial concentration of the oil, b that of the autocatalyst, and x the amount of the oil oxidised.

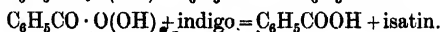
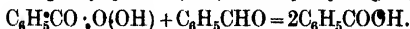
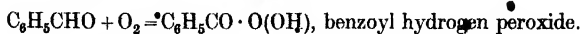
It is possible that the autocatalyst is a higher peroxide than that found in linoleyn. There is an induction period in the curves in Figs. 10 and 11 which disappears in the presence of siccatives or at a higher temperature of drying. It must be pointed out that in any study of the rate of oxidation the experiments must be carried out with due regard to the decomposition products, as in Genthe's work. From the above equation there must be a quantitative relationship between the quantity of linseed oil oxidised and that of the autocatalyst simultaneously generated. The autocatalytic peroxide supposed to be formed is analogous to that produced in the oxidation of a metal in the presence of water:



in the oxidation of phosphorus:³

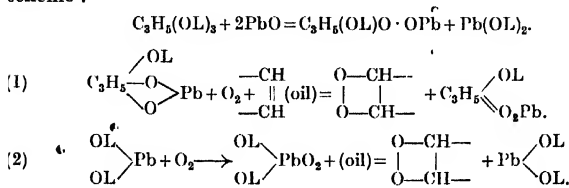


or in the oxidation of benzaldehyde:⁴



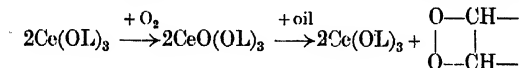
Ingel⁵ showed that the driers remove the induction period and shorten the time of setting and drying. Taking a typical drier as a compound of lead and of manganese, the first question which arises is as to whether they act directly as catalysts, taking up oxygen and passing it to the oil with the formation of the glyceryl peroxide, or whether they stabilise the presence of the autocatalytic peroxide and thus exert a pseudocatalytic function.

Ingel⁵ expressed the mechanism of drying by the following scheme:



In the first case there is an intermediate substance produced giving rise to a peroxide oil, whilst the lead has assumed a higher degree of oxidation in the second case.

That metals assume a higher degree of oxidation during the process is instanced by the behaviour of cerium tungate on oxidation,



The existence of higher oxides has been indicated and the formation of ceric salts in varnishes containing a cerium drier can be observed in the change of colour to yellow (the usual colour of ceric salts). It would appear as if the drier took the place of autocatalyst, assuming the autocatalyst to be an unstable higher peroxide than is present in linoxyn.⁶ Driers differ in their power to accelerate the drying of linseed and other oils. Linseed oil, which ordinarily takes three days to dry as a thin film, will dry in five to eight hours in the presence of 0.5 per cent lead and a trace of manganese.

Many other metals show a similar accelerating action.

Fokin⁷ places such metals in the order given in the list, beginning with the strongest drier:

Co, Mn, Cr, Ni, Fe, Pt, Pd, Pb, Ca, Bi, Ba, Hg, U, Cu, Zn.

The velocity of drying is stated to increase with the cube root of the concentration of the catalyst metal, but it seems unwise to develop a relationship between reaction velocity and concentration without consideration of the superficial concentration.

Ingall⁸ gives the time of drying (when the film becomes dry to the touch) of linseed oil films (0.001-0.003 in. thick) containing 2 per cent of resinsates of the following metals, and the increase in weight of the films at different periods:

Linseed oil containing :	Mn.	Pb.	Zn.	Ca.	Co.	Cu.	Fe.	Al.	Cr.	Linseed oil alone.
Drying times, hours :	12	26	30	32	36	46	60	85	95	121
Percentage increase in weight after 12 hours :	17.4	9.4	6.5	6.0	5.9	4.9	4.1	2.8	2.0	0.933

Vanadium resinate is stated to be a better drier than manganese, but inferior to cobalt resinate.^{8a}

It is well known that the films continue to harden progressively for a long and indefinite time after the drying time as given.

Mackey and Ingle⁹ classify metals in the following order of drying :

Co, Mn, Ce, Pb, Cr, Fe, U, Na, Ag, Zn, Hg, and Al.

The method employed is novel ; cotton-wool, soaked in linseed oil containing the metal to be classified, was placed in a cloth-oil tester,¹⁰ and the time taken to attain a temperature of 200° C. was noted. In the case of cobalt that temperature was attained in the shortest time.

The proposed arrangement of the metals in the order of drying is not satisfactory. From the lists given it appears that a metal which can form more than one oxide acts as a drier or oxygen carrier when it is in an oil soluble form, provided that the salts of the lower oxides are more stable than those of the higher oxides. It has also been stated that the more oxides which a metal can form the greater will be its catalytic activity.

Gardner,¹¹ in his experiments on the effects of moisture on drying oils and varnishes, states that a surprising feature of the results is the very high apparent efficiency of aluminium compounds as driers. Although slow in initial effect they seem to have an even greater drying power than the corresponding compounds of lead. Further investigations with aluminium salts as driers are advisable before the more general impression is put aside, although the writer can confirm the drying power of aluminium resinate. Much depends on how the efficiency of a drier is stated, either as increase in weight of the film, rise in temperature, or actual drying time. The usual method of testing the drying power is that of the craftsman who fixes the time when the film becomes satisfactorily dry to the finger, which condition is preceded by a "dust-dry" period. Rough though the method is, with a personal error of half an hour and a dependence on light, temperature, and hygrometric conditions, it is satisfactory for practical purposes in the hands of a skilled worker.

The results of the gain-in-weight trials on oxidation of an oil may be considered as deciding broadly between drying and non-drying oils or between metals as "driers," but in practice the rate of oxidation is not sufficient to establish the use of the metal as a "drier." Rapid setting and hard drying throughout the film from top to bottom, without rivelling or silkiness or a dry surface layer with a soft undercoat, are necessary to establish a metal as a satisfactory drier.

The metals in the lists given may be employed as (a) in a finely divided state (Livache proposes finely divided lead); (b) oxides

(lead, manganese, and iron inumber); (c) acetates (lead, cobalt, and manganese); (d) borates (lead, manganese, and cobalt); (e) metallic salts of drying oils (linolates, linolenates, tungates, and even oleates); (f) resinates of the metals (lead, manganese, and cobalt). The oleates of lead, manganese, and cobalt may be used as driers, but they are not so readily soluble nor so active as linolenates or linolates. There is the tendency to consider salts of $C_{18}H_{32}O_2$ and $C_{18}H_{30}O_2$ acids as yielding most of the drying power, but their solubility must be carefully considered, because the form in which the metal is presented often determines its selection; e.g. nitrates and chlorides are seldom used as driers, whilst acetates and borates are good driers, especially borate of manganese, which, however, requires rather a high temperature to yield its maximum effect. Lead stearate is of little use compared with lead linolenate or linoleate. Lead tetraethyl, which is a clear and nearly water-white liquid containing 70 per cent of lead, freely soluble in linseed oil, is stated to be useless as a drier at the ordinary temperature. It is evident that the metal must be present in a suitable form, because finely divided lead, in spite of its apparent insolubility in linseed oil, and although soluble in the acids which are present in very small quantity in the oil, has shown itself in the hands of Livache to be a good drier. Manganese, one of the best driers, gives a coating which often shows rivelling, and cobalt films show the same defect, due to rapid surface oxidation. The lead films are rounder and fuller. Mulder states that lead gives films "tough like rubber," while manganese produces films "tough like leather," although lead is a slower drier than manganese. The drying time of linseed oil with a suitable drier can be brought down to seven or eight hours, for which 3.5 parts of manganese or cobalt to 10,000 of oil will suffice. The films must be about 0.002 in. thick and the temperature about 75° F. It is evident that the action of the metallic drier is specific, and it will be of advantage to consider the forms in which metallic driers are used in practice, beginning with manganese.

Manganese Driers.—The United States Bureau of Mines has issued a pamphlet on the use of manganese salts as driers, and details as to their manufacture and of other metallic driers are given in a pamphlet by H. A. Gardner and R. E. Colman.¹² The manganese compounds used as driers are the sesquioxide (Mn_2O_3), pyrolusite (MnO_2) or the black oxide-hydrate, borate, resinate, linolenate, oxalate, and a few other salts. Manganese dioxide (natural and artificial) is employed extensively as a drier by dissolving it in linseed oil at 500° F. Not more than $\frac{1}{4}$ lb. per cwt. of oil is used. It may dissolve partially as linoleate,* but the boiled oil produced is dark in colour.

Manganese sulphate is prepared on the large scale from the dioxide by heating to redness with ferrous sulphate and then dissolving out the manganese sulphate with water. It is largely used by oil-boilers for preparing pale boiled oils, and is also the source of the oxalate and borate.

* Linoleate is a term used to include a mixture of linolate, linolenate, and oleate obtained from linseed oil.

Manganese borate is formed by adding a solution of manganese sulphate to a hot solution of borax, from which it is precipitated. The oxalate is made by adding a solution of sodium oxalate to a soluble manganese salt.

The resinate, linoleate (8.9 per cent Mn), and tungate (9.3 per cent Mn) are made by adding a manganese salt to a solution of a rosin soap or an oil soap respectively, or by heating manganese acetate and rosin to give manganese resinate. They are soluble in turpentine and in white spirit, but the solutions darken rapidly on keeping to a deep claret colour. One lb. of the linoleate mixed with 5 lb. of linseed oil, which is then added to 10 galls. of linseed oil, is said to form a good drying oil. It must be stated that these salts are more efficient if they are dissolved in a medium as soon as possible after preparation, because their solubility depreciates on keeping, due to oxidation giving rise to less soluble products.

Cobalt Driers.—Cobalt is used in the form of acetate, resinate, linolenate (9.5 per cent Co) or tungate, and the driers are prepared from a soluble cobalt salt (*e.g.* sulphate) in the same way as the corresponding manganese compounds. The cobalt drier solutions are as highly coloured as those of manganese, but they do not darken a mixing to the same degree, and are highly coloured compared with the corresponding lead compounds. As the quantity of the metal used is very small, a cobalt-treated oil will bleach out on drying. Comparison of cobalt with manganese and lead will be referred to under "Combinations of Driers."

Lead Driers.—Lead is used as oxide (flake, massicot) or as red lead; generally flake litharge is preferred. It is sometimes introduced as flake litharge into a varnish mixing directly in the "drumming" process, or else in the form of a soap produced by dissolving the oxide in oil. It may be used in the form of acetate in conjunction with rosin to give a resinate (25.6 per cent Pb). It is preferable to use the oxide dissolved in the oil rather than in the form of separately prepared linoleate (27 per cent Pb), because of the difficulty in drying the very viscous salt. It must be mentioned that solutions of lead soaps will deposit lead stearate and palmitate on standing or on thinning.¹³

Red lead and manganese dioxide require a temperature of 300°-500° F. for their solution and produce dark-coloured oils which on continued cooking (not too long) give an almost black mass, which is soluble in turpentine and is the basis of the so-called Japan or Japan driers. They are as powerful as the precipitated linoleates, and have been known for a very long time. Special kinds for many purposes contain resins, but the catalytic power is not increased thereby.

Cerium Driers.—It is stated by some investigators that cerium linoleates are inactive. From the writer's experience this is incorrect.¹⁴

If cerous oxalate be made the starting-point, it can be easily transformed into cerous linoleate, which dissolves readily in oil, giving a clear solution without the separation noticeable in the

case of lead linoleate. In drying power it is to be compared with lead linoleate, and it is of the same or slightly greater activity, but it needs a second drier, such as manganese, or a promoter to be present; e.g. manganese and cobalt.

10.4 oz. of Ce_2O_3 to one gallon of varnish mixing, to which has been added a trace of a soluble manganese drier, will dry better and quicker than when a chemically equivalent amount of lead is used.

The behaviour of the film of the cerium mixings is markedly different to that of the lead varnishes. They remain soft up to the last hour of drying, when a very rapid setting occurs, showing that the metal is not a surface drier. The hardness next day is as good as that of a lead varnish; moreover, there are no bottoms as in the case of lead varnishes and no blooming in "long oil" mixings. Owing to the oxidation of the cerous salts to the ceric form, the varnishes become yellow in time, assuming the characteristic colour of ceric compounds.

It is because of the necessity for a second drier that writers have dismissed cerium as inactive, although Mackey and Ingle place it third in their list of drying metals as tested by the cloth oil-tester.

Combinations of Driers.—The metallic content of boiled oils and varnishes stands in no stoichiometric proportion to the mass of the oxidation product. According to Weger,¹⁵ the drying power of manganese increases up to a concentration of 0.2 per cent., but further increase causes no acceleration on drying (cf. Bach, Oxidation of HI by hydrogen peroxide in the presence of peroxidase).¹⁶

Lippert¹⁷ states that the combined oxygen is increased by the presence of small quantities of manganese, but if the amount exceeds 0.2 per cent the oxygen number falls.

There is, moreover, an undoubted advantage in the use of mixed driers as shown in combinations of lead and manganese. In illustration reference may be made to results obtained by W. Flatt¹⁸ and by Sternberg, who found that the drying power of lead linoleate increases with the content of the lead oxide up to 1.9 per cent lead; the drying power of manganese is at its maximum with a concentration of 0.1 per cent of the metal. The optimum concentrations of lead and manganese are 0.77 per cent and 0.002 per cent respectively. Meister¹⁹ states that 0.12 per cent Mn, 0.45 per cent Pb, i.e. 1:4, are the best when the metals are in the form of resins. Manganese resin contains 6 per cent Mn; lead resin 22 per cent Pb; zinc resin contains 7 per cent Zn; cobalt resin 4.5 per cent Co. The best results are obtained when 1.5 per cent manganese and lead resins are dissolved in linseed oil, whereby the drying time is reduced to six hours. In a 2 per cent mixture of these metals, in the form of resins dissolved in linseed oil at 150° C., the following drying times were obtained:

Drying times: Mn, Pb, and Ca, 6 hours; Mn, Pb, and Zn, 7 hours; Mn, Zn, and Ca, 9 hours; Mn, Zn, and Co, 7 hours; Pb, Zn, and Ca, 9½ hours; Pb, Zn, and Co, 8½ hours.

The addition of lime in neutralising the acids in the oil must also favour any polymerisation during the drying.

W. Flatt¹⁸ considers that excess of drier in the case of manganese or cobalt does not retard drying, and quotes the following observations :

Linseed oil 1.00 per cent Pb dried at 10° C. in 20 hours.

•	"	0.25	"	Mn	"	"	16	"
"	"	0.08	"	Co	"	"	4	"
"	"	0.25	"	Co	"	"	4	"

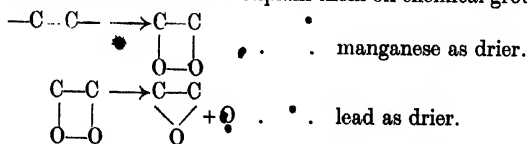
Weger (*loc. cit.*) stated that 0.25 per cent Mn or 0.5 per cent Pb and 0.1 per cent Mn were the optimum amounts; excess was no advantage, but did not retard.

The following table gives the results of Flatt's experiments with mixed driers, using percentage as given :

Pb.	Mn.	Co.	Drying Times.
Per cent.	Per cent.	Per cent.	Hours.
1	20
$\frac{1}{2}$..	$\frac{1}{4}$	16
$\frac{1}{3}$..	$\frac{1}{2}$	16
$\frac{1}{4}$..	$\frac{3}{4}$	16
..	1	..	24
$\frac{1}{4}$	$\frac{3}{4}$..	17
$\frac{1}{2}$	$\frac{1}{2}$..	16
$\frac{1}{2}$	$\frac{1}{4}$..	18
..	$\frac{1}{4}$	$\frac{3}{4}$	17
..	$\frac{1}{2}$	$\frac{3}{8}$	18
..	$\frac{1}{2}$	$\frac{1}{2}$	19
..	$\frac{3}{4}$	$\frac{1}{2}$	20

¹ From the figures given the manganese drier does not stimulate the cobalt drier, but rather the reverse. Nevertheless, there is evidence that even in the case of these two metals there is some mutual influence. Consensus of opinion is in favour of mixed driers, Pb and Mn, and even cobalt and manganese. Lead driers are less sensitive to temperature variations, whereas manganese driers are the most sensitive. There is always an increase in viscosity of lead drying oils, whilst manganese and cobalt oils change only very slightly; nevertheless, a manganese drying oil improves with age.)

It is evident that the activity of the drier depends specifically on the metal. Roohs²⁰ seeks to explain them on chemical grounds :



When there is a combination of the two driers, a peroxide glyceride of the Orloff type (p. 17) would be formed.

Another view is that the second drier acts as a polymerising

agent causing a union of unsaturated molecules and preventing the oxidation being carried so far as the production of Reid's superoxidised oil.²¹ The softening of linxyn may be due to a return of the gel to the fluid state.²² This view is very worthy of consideration, especially as aluminium has been found to give greater drying powers than the corresponding compound of lead; moreover, the advantages of lead as a drier are not so manifest when dealing with polymerised or easily polymerised oils (cf. percentage of linoxyn formed when lead and manganese driers act on lithographic oils compared with manganese alone (Morrell, *loc. cit.*)). No doubt it is advisable to check excessive formation of peroxide glycerides, which are over-prone to subsequent decomposition, and the combination of metallic glycerides may be favourable in this respect. It is sometimes stated that driers lose their activity. Undoubtedly certain driers cause a thickening of a varnish, which may dry more slowly owing to increased thickness of the film, but as long as there is no separation of the drier and the fluidity is maintained, the drying time in the case of varnishes remains steady.

Theories of the Action of Driers.—The metallic driers are catalysts, and the term catalysis as defined by Henderson (*Catalysis in Industrial Chemistry*, 1919) is more generally used to designate those chemical changes of which the progress is modified by the presence of a foreign substance; the agent which produces the effect is called the catalyst.

The theories advanced to explain the action of catalysts in the drying of oils and varnishes fall into two classes: (a) chemical; (b) physical.

(a) *Chemical Theories.*—These have been already indicated. Without the drier it is presumed that a higher and unknown peroxide of the glycerides is formed which is subsequently reduced.* When linseed oil is boiled without driers it is oxidised very slowly, but its activity is regained when air is blown into it. The metal of the drier stimulates the formation of a peroxide which undergoes subsequent and slow change, either by reduction to an oxide owing to the reaction with unoxidised oil, or by polymerisation of the peroxide or oxide oil, or by partial decomposition of the molecule; all three types occur simultaneously, but at different rates depending on the general conditions and on the nature of the metal in the drier.

- (1) $\text{XO}_2 + \text{X} = 2\text{XO}$ without driers. (2) $\text{X} + \text{O}_2 + \text{drier} = \text{XO}_2$.
 (3) $\text{XO}_2 + \text{X} = 2\text{XO}$. (4) Polymerisation of $\text{XO} + \text{XO}_2$.
 (5) $\text{XO}_2 + \text{H}_2\text{O} = \text{XO} + \text{H}_2\text{O}_2$. (6) Decomposition products of XO_2 .

If the action of driers is simply catalytic, i.e. if they act as oxygen carriers, then the oxygen absorption for a given oil ought to be a constant quantity. Coffey²³ found that the oxidation curves for linseed oil with or without drier show that the rate of

* The part played by moisture during the oxidation of linseed oil must not be overlooked. It is possible that $\text{X} + \text{O}_2 + 2\text{H}_2\text{O} = \text{X} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{O} \end{smallmatrix} + \text{H}_2\text{O}_2$ (p. 33)

may occur.

main oxidation is unaltered, but that the oxygen absorption recorded in the presence of drier is lower than that observed when no drier is present; moreover, the reaction curves are different.)

The true oxygen absorptions, when the following catalysts were dusted in the solid form on a film of linseed oil, are: Cobalt oxide, 25 per cent; lead oxide, 17 per cent; manganese borate, 23 per cent; red lead, 17 per cent; lead acetate, 24 per cent; linseed oil without driers, 28.7 per cent (Fig. 11c).

The induction period is shortened in the presence of driers, but the final oxygen absorption is lowered. The oxidation curves do not run parallel with the curve for oil alone, and deviate considerably from the logarithmic curve suggested by Fokin. Carbon dioxide is evolved whether the driers are present or not. (No trace of hydrogen peroxide was observed when the driers were present.) It is evident that the presence of the drier modifies the course of the oxidation of the oil, and it does not act as a catalyst in the strictest sense. (The action of the secondary drier, *e.g.* lead, would appear to be that of coagulator of the oxidised product whose formation has been accelerated by the primary drier (manganese and cobalt).)

(b) *Physical Theories*.—How far are oils and varnishes to be considered homogeneous systems in which the reaction is proportional to the concentration of the catalyst? The properties of surfaces must be considered, so that drying belongs essentially to the consideration of heterogeneous systems, and the adsorption views of Faraday (1833) as to catalytic activity are relevant.

The surface of the drying oil is a zone in which various possible intermediate compounds and final products are capable of existence side by side and in which the actual equilibrium state would be such that there was a definite proportion between these possible intermediate products in a kinetic sense; but, while the actual number of molecules of each species remained constant, the individuality of these molecules would be continually changing. It is possible to see how manganese or cobalt could help the absorption of oxygen by linseed oil, by reason of the fact that among the various possible compounds formed on the surface of separation there would be peroxides, in which oxygen was at a potential sufficient to be transferred to the oil. It is evident that the chemical proportion of driers will not account fully for their behaviour, and the study of their surface energies is of importance. The rates of diffusion of the oxidation products depend on the viscosity of the material, and must be taken into account if the evil defects of surface drying are to be overcome. Polymerisation of the products and change in their dispersion in the film are factors which are influenced by the nature of the drier. It is therefore difficult to make a strict comparison of driers as catalysts. Driers may be considered as promoters absorbing oxygen selectively on the surface, followed by chemical combination. (There may be differences in the surface energies of the dissolved driers (there would appear to be differences between those of lead, manganese, and cobalt) which will affect powerfully the course of the change.)

According to the report of the Contact Catalysis Committee of the American National Research Council the catalytic agent activates one of the reacting substances, whilst the promoter activates the other. The phenomena are essentially those of adsorption with formation of indefinite intermediate compounds.²⁴ On the hypothesis of directive and selective adsorption, connection may be made between the intermediate compound theory and the adsorption theory, because the idea of a directive force assumes chemical union between the surface of contact and the molecules of the surrounding medium. The distinctive character of the interfacial molecular condition has been put forward by Langmuir,²⁵ who assumes that a solid catalyst becomes coated with a single layer of molecules by adsorption; such condensation is accompanied by a change in the character of the adsorbed molecules, involving a dissociation of elementary molecules (*e.g.* oxygen into atoms) by which the atoms of the condensed molecules are definitely associated with certain molecules in the surface layer. The application of Langmuir's theory by Lewis²⁶ in terms of the radiation hypothesis involves the condensation of the catalyst in the atomic form on the surface. It must be remembered that substances of a colloid nature are present in drying oils, varnishes, and paints, and the activity of metals in such solutions is vastly different from what it is in aqueous solutions. A more careful study of Livache's method of drying by finely divided metals would establish a closer connection with the phenomena observed when unsaturated oils are reduced by hydrogen in the presence of metallic catalysts. It is for the chemist to decide, from the examination of the products of oxidation, the chemical changes which have occurred. It would appear that the activity of driers is to be attributed to causes put forward by both theories taken together.

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CHAPTER III

BOILED, BLOWN, AND STAND OILS (LITHOGRAPHIC VARNISHES)

It is advisable here to draw attention to the differences in the nomenclature of varnishes in England, France, the United States of America, and Germany. In America the term boiled oil has the same meaning as in England. In France it is *huile de lin cuite*, in Germany *leinolfirnis*, comprising drying oils with thinners. The terms varnish and *vernis* are applied to solutions of resins in a solvent or solvents with or without drying oil. In Germany the term *lackfirnis* is used, which is specialised under separate terms, such as *flüchtige lacke*, including the English spirit varnishes, or *fette lackfirnisse* or *fette lacke* (*al-lacke*), which contain copal or a resin, drying oils and thinners, and are the equivalent of the English oil varnishes.

Boiled Oil.—The operation of boiling oil is one in which great secrecy is observed by manufacturers. When linseed oil is heated to 220°-280° C. (300°-500° F.) for several hours in contact with air, its drying properties are increased. It is customary to add small quantities of metallic driers, whereby the resulting boiled oil is essentially an oil containing a metallic catalyst. Controversy rages over the merits of "kettle-boiled" oil and "bung-hole oil," i.e. oil in which the driers have been incorporated by heat compared with linseed oil to which driers, soluble at a low temperature, have been added. In the boiling of linseed oil there is always a darkening in colour, but a light coloured oil is often required, in order that the oil may not unduly discolour pigments suspended in it. It has become the practice to make a drying oil with metallic oxides by heating with a small portion of the oil until they are dissolved, and adding the smaller quantity of oil so treated to the bulk of the oil, which is maintained at a much lower temperature, usually not above the boiling point of water. The resulting oil is light in colour and there is considerable saving in the cost of fuel, time, and labour. The oil-boiler may buy his driers from the varnish maker, often to the detriment of his oil, unless he carefully examines the composition and quality of the driers offered, which may be lead and manganese resinates incorporated at 150°-160° C., or even at a lower temperature, in contradistinction to the boiled oils in which lead oxide or manganese oxide are dissolved at 220° C. The demand is for a

boiled oil which has been heated at some stage of the process, but it is undoubtedly correct that for certain purposes, especially where colour is of importance, the use of oils of the bung-hole type is quite satisfactory. McIlhenny maintains that, provided proper materials have been used, lower-temperature drying oils as good as the kettle-boiled oil. The temperatures required for the incorporation of driers in linseed oil are given below :

Drier.	Amount used (percentage).*	Mean Temperature.
Manganese dioxide (Braunstein)	0.5	250° C.
Hydrated manganese oxide	0.1-0.2	170°-220° C.
Manganese borate	0.5-1	Ordinary temperature
Flake lead	0.5-1	" "
Lead acetate	1-2	" "
Manganese acetate	0.5	" "
Lead resinat fused	1-3	120°-150° C.
Manganese resinat fused	2-3	Ordinary temperature
Manganese linoleate	1	150° C.

Method of Manufacture.—The oil may be heated over a fire in large boilers holding 100-600 gallons.

The boilers are made of wrought-iron plates of the form shown in Fig. 12, and the bottoms, which are made separately, are riveted

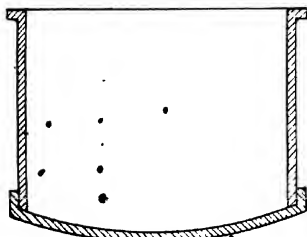


FIG. 12.—Oil-boiling pan.

to the sides. The corroding action of the fire is greatest on the bottom of the boiler, which must thus be easily replaceable. The boilers should be set over furnaces with fireplaces outside the boiling shed. A suitable cover should be fixed on the pot so as to allow both ingress of air and the removal of irritating and acid fumes from the boiling oil. The oil in the pot (which should be not more than two-thirds full)

is carefully heated up to 240°-280° C. Caution must be exercised at first, otherwise the oil may boil over owing to the presence of water and mucilage. After a time the oil "boils" quietly and is kept at 280° C. for not less than two hours. After the boiling has proceeded for half an hour the driers are added from time to time in small quantities. The time of boiling and the quantities of driers vary, but generally 5 lb. of lead oxide per ton of oil and five and a half hours are deemed sufficient.* A French ordinary boiled oil may contain 6 per cent of litharge, which is added to the oil heated to 150° C. and the temperature raised to 230°-240° C. The cold clear oil is drawn off as "boiled oil" and the foots

* War Office Specification for boiled linseed oil, C.W.D./405, 1920, limits the percentage of lead to 0.5 per cent, and of cobalt or manganese to 0.05 per cent. * Am. Soc. Test. Materials adopted in 1915 for boiled oil 0.1 per cent lead and 0.03 per cent manganese.

are used for putty or mixed into cheap paints. A strong French boiled oil may contain 10.25 per cent litharge and 0.75 per cent umber added at 250° C. and the temperature then raised to 270° C. and kept there until the desired consistency is obtained. (A clear boiled oil may be made by incorporating 1.75 per cent red lead, 1.5 per cent umber, and 1.5 per cent quicklime. The red lead is added at 170° C., then the umber, and the temperature is raised to 230°-240° C., the lime being stirred in after removal of the oil from the fire (Coffignier). The oil darkens in colour during the boiling, owing to the formation of decomposition products depending on the temperature of boiling and the nature and quantity of the driers used. Manganese dioxide produces a darker colour than that produced by litharge. Lead and manganese acetates or manganese oxalate produce the palest oils. The temperature of the boiling process should be kept as low as possible to prevent darkening. The loss in weight is very small, amounting to not more than one half per cent in the case of a lead-boiled oil of fourteen hours' heating. The direct heating of linseed oil over a fire may be replaced by steam heating. The oil is run into a tank fitted with a closed steam coil and heated for about two hours at 95°-97° C. This preliminary treatment assists in the coagulation of the mucilage, and reduces the frothing of the oil during the later stages of the process. The hot oil is run into a steam-jacketed boiler provided with a stirrer and air inlet, as shown in Fig. 13. The oil is heated and air is blown through it. The driers are introduced from time to time, and on completion of the process the oil is run into settling tanks.¹ The oil-boiling plant supplied by Messrs. Rose, Downs & Thompson is on the same general principle, differing only in mechanical details. Boiled oils may be prepared by heating *in vacuo* or under reduced pressure to avoid darkening.² During the boiling, oxidation occurs with improvement in the body and gloss of the oil. It must be pointed out that the peroxide of the more active components may cause oxidation, and polymerisation of the less unsaturated glycerides with accompanying thickening. Boiled oil is of a brown

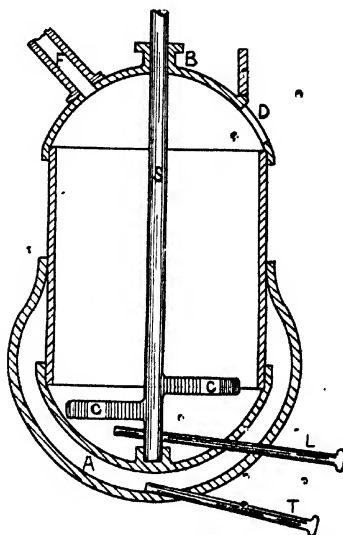


FIG. 13.—Steam-heated oil-boiler. A, steam jacket; B, centre for vertical shaft; C, agitators; D, oil inlet; F, flue; L, air into oil; S, vertical shaft; T, steam inlet.

colour of varying depth of shade. Its odour is characteristic and peculiar, and differs from that of raw linseed oil. The specific gravity varies between 0.933-0.952, depending on the mode of manufacture. Exposure to light is stated to darken the oil, although linseed oil is bleached under similar circumstances. The properties which the consumer requires are consistency, cleanness, drying power and freedom from added impurities; *e.g.* rosin, rosin oil, mineral and vegetable oils. The drying time varies from five to twenty hours. Boiled oil gives a hard, lustrous film, which is liable to crack on exposure to air, so that raw oil is added to improve the elasticity. The experience of painters and linoleum printers using raw oil and a drier instead of boiled oil in their work has shown that it cracked and blistered badly (Ingle).

The following table shows the changes which occur during the drying of a film of *cold-boiled* oil by spreading it on a sheet of glass, exposing to the air and scraping off portions at intervals for analysis. The films were examined by the method described on page 50. The oil (original iodine value 183), containing 1 per cent of lead driers, was "boiled" in bulk at 86° C. by blowing in air, the sp. gr. of the product being 0.966.

	Oil before Exposure, (1 per cent lead driers.)	Oil after Drying at 86° C.			
		3 Days.	5 Days.	7 Days.	10 Weeks.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Unoxidised oil . . . (see below)	100	45.7	33.9	10.9	17.5
Partially oxidised oil . (see below)	..	52.5	50.1	43.6	28.9
Linoxyn . . . (see below)	..	1.8	16.0	45.5	53.6
Unoxidised Oil—					
Unoxidised acids . . . (calculated to oil)	87.1	35.5	24.5	9.2	13.35
Oxidised acids . . . (calculated to oil)	12.9	10.2	9.4	1.7	4.15
Partially Oxidised Oil—					
Unoxidised acids . . . (calculated to oil)	..	14.6	10.0	17.2	9.5
Oxidised acids . . . (calculated to oil)	..	37.9	40.1	26.4	19.39
Linoxyn—					
Unoxidised acids . . . (calculated to oil)	4.9	12.6	7.34
Oxidised acids . . . (calculated to oil)	11.1	32.9	46.26

Half the oil becomes partially oxidised oil, soluble in methylated ether, but insoluble in light petroleum. Linoxyn increases at the expense of the partially oxidised oil fraction. At a certain point the quantity of unoxidised oil increases. Linoxyn is not a

simple substance, but contains glycerides of oxidised and other acids.)

Blown Linseed Oil.—Linseed oil can be thickened by oxidising in a current of air blown through it, and it may be artificially aged thereby. Generally the oil is heated to 121°-149° C. (Hazura states 66° C., and Ingle 60°-100° C.) and a large volume of air blown in, the air passing into the oil through small perforations in a pipe of about $\frac{1}{4}$ in. diameter. The temperature should be held at 188°-205° C., but it may be necessary to cool the oil by a water-jacket to prevent rise of temperature due to oxidation. After a few hours the oil begins to fume strongly, and the head must be beaten down. The air blown in may be heated previously to 205° C. in a superheater, and the oil may be blown without further heating. When blown with hot air the oil dries better and is of paler colour, but is more liable to gel during the process of manufacture than when heated and cold air is passed in. It is advisable to provide the pan with a steam jacket, so that if the operation is not continuous the thickened oil may be rendered fluid to permit the resumption of the introduction of the air. To oxidise 600 gallons of linseed oil Sabin states that air from a rotary pump with a 3-in. outlet running 225 r.p.m. may be passed in for about forty to fifty hours without causing coagulation. If the blowing be stopped a little short of gelation the oil can be carefully thinned while hot (108° C.) with turpentine or white spirit, or it may be stored in an open tank ready for use. Its viscosity is so high that it will not pour and must be dipped out. The increase in weight is about 10 per cent. The oil dries by itself, but the rate of drying is accelerated by addition of driers. Owing to its high viscosity it may be used to confer durability on cheap linseed oil rosin varnishes, and it may also be incorporated with China wood oil. In the blowing of linseed oil the molecular weight appears at first to be lower than that of the original oil, but this is due to decomposition having ensued. If the fatty acids from the drying oils be blown, 50 per cent of the acids (after removal of the oxyacids by petrol ether, the volatile acids by steam, and the saturated acids by freezing out) showed a molecular weight of 423 (280 would be the normal molecular weight). It is evident that intramolecular polymerisation has occurred either directly or through the medium of oxygen. At higher temperatures, *e.g.* 230° C., ordinary bimolecular polymerisation occurs.³ The primary oxidation products are completely soluble in light petroleum, but after saponification petroleum-insoluble oxyacids are obtained.⁴ These oxidised acids of Fahrion are of interest because of their insolubility in petroleum ether. Ingle⁵ considered that they were very probably decomposition products, mainly of a resinous character, formed in the aldol condensation of the aldehydic groups produced by the action of alkali on the peroxides during the saponification. He thought that the evidence of polymerisation occurring at such low temperatures as 60°-100° C. was not convincing. If polymerisation does occur at such low temperatures it would be expected to take place by

polymerisation of the molecules by attachment through the peroxide oxygen. The action of ageing and heat on a semi-oxidised oil produced by blowing in air at 140°-212° F. (60°-100° C.), or by exposing linseed oil in a fine spray to air at that temperature, has been investigated by Ingle (*loc. cit.*). It may be taken as typical of methods used for investigation of oxidation products of the oils and given in some detail. The ether insoluble part is linoxyn. The ether soluble part after removal of the solvent gives a part soluble in petroleum ether, viz. unoxidised oil, and a part insoluble, viz. partially oxidised oil. Each portion was saponified and the oxidised acids examined by Fahrion's method. The results are given in the following table :

	Freshly Oxidised Oil.	Five days after.	After Heating to 165° C.*	Heated Material analysed after Thirteen Months at the Ordinary Temperature.
Linoxyn	27.3	31.3	36.7	45.3
Partially oxidised oil . .	53.2	44.6	40.0	34.5
Unoxidised oil	19.8	23.2	23.4	21.7
Iodine value	70.5	70.5	64.5	..
Loss in weight on heating	2.5	..
Partially Oxidised Oil—				
Oxidised acids	27.7	23.2	..	19.5
Unoxidised acids	14.0
Unoxidised Oil—				
Oxidised acids	4.0	4.0	4.8	4.2
Unoxidised acids . . .	15.3	16.3	18.2	16.6
Total oxidised acids . .	39.6	..	41.3	..
Total unoxidised acids .	42.0	..	42.5	..

* At this temperature the oil "turns," i.e. passes from the liquid to the semi-solid.

The linoxyn on saponification gave 83 per cent acids soluble in methylated ether containing 72 per cent oxidised acids (I.V. 55.0) and 11.0 per cent unoxidised acids (I.V. 92.5).

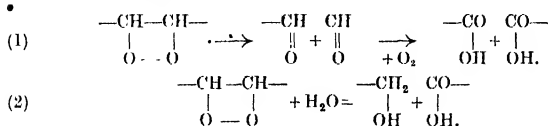
Ingle concluded that under the above conditions age increased the quantity of linoxyn in the oil at the expense of the partially oxidised oil. It also increased the amount of the unoxidised oil, while the iodine value remained the same. The oxidised acids in the partially oxidised oil decreased. There seems to be no evidence of autoxidation, as no decrease in the iodine value is observed (the change, in the writer's opinion, indicates gelatinisation).

Heating increases the linoxyn, reducing the partially oxidised and slightly increasing the unoxidised oil.

With reference to the durability of coatings containing blown oil there is a difference of opinion. Generally the polymerised oils give more durable coatings. If in the oxidation a high proportion of peroxides is left in the oil, it may on weathering be expected to yield the superoxidised oil of Reid⁶ to the detriment

of durability, but if an oxide $\begin{array}{c} \text{C}-\text{C}^{\bullet} \\ \diagdown \diagup \\ \text{O} \end{array}$ were attained, durability would

be expected. The superoxidised oil of Reid is considered by Wegner ⁷ to be a reversion of gelation of linoxyn to the semi-fluid condition. The oxidised oil produced by blowing or by cold boiling after the formation of peroxides (drying process) would be decomposed by lengthy exposure with the formation of fluid acidic products according to one of the schemes :



These products may be neutralised by bases, as in the case of lead white or whiting, to form more or less brittle coatings, but if the paint consists of inert pigments, such as china clay, barytes or iron oxides, the films will be sticky, and easily removable. The same greasiness due to the formation of acidic decomposition products occurs in the manufacture of linoleum by the oxidation of linseed oil in the presence of manganese driers in the Walton shower bath.

Absorption of Oxygen by Raw, Boiled, and Polymerised Oils.—

The table on following page shows the absorption of oxygen by raw, boiled, blown, and polymerised oils (Morrell and de Waele, p. 63).

There are many patents dealing with the blowing of drying oils. Brin's Oxygen Co. blow in pure oxygen.⁸ Andreoli⁹ ozonises the air previous to blowing it into slightly warmed linseed oil, and to prevent over-oxidation a certain quantity of hydrocarbons (b.p. above 100° C.) or grease is added. Electrolysis by dilute sulphuric acid in an emulsion of oil, and the addition of sodium peroxide to facilitate the oxidation without addition of any other drier (Bernet), have also been proposed.

The oxidation by air in ultra-violet light has been tried, and Marcussen¹⁰ has described a method for thickening oils by silent discharge to produce Voltöle. Rape and fish oils are first thickened by blowing in air, and then electrically treated as shown in Fig. 14. The glass and metal plates are a few millimetres apart.

The operation is carried out under reduced pressure ($\frac{1}{10}$ atmosphere), using 8-10 kilowatts current.

The effect of passing ozonised air into linseed oil at the ordinary temperature is essentially to bleach the oil, and the process will be described under the "Refining of Linseed Oil."

In practice the danger of spontaneous ignition during the blowing is avoided by heating the oil for a long time at 150°-260° C., so as to allow polymerised flakes to settle, and decanting off the clear oil before blowing. The flocculation of linseed oil in the

THE APPARENT ABSORPTION OF OXYGEN BY RAW, BOILED, BLOWN, AND POLYMERISED OILS

	(Increase in Weight.) [Cf. Andé's <i>Drying and Boiled Oils</i> , 1901.]			
Olive oil (in winter time).	0.67% in 2 days	1.58% in 5 days	3.39% in 12 days	5.6% in 24 days.
Baltic linseed oil (winter).	3.8% „ 3½ „	13.6% „ 6½ „	17.62% „ 8½ „ (maximum)	
China wood oil (winter).		11.73% „ 6½ „	13.46% in 8½ days (maximum)	
East Indian linseed oil (summer).	15.9% „ 3½ „	16.3% „ 6½ „	14.2% in 9 days	
East Indian linseed oil thickened 500-530° F. 32 hours (winter).	0.56% „ 3½ „	2.0% „ 6½ „	2.62% „ 8½ „	10.9% „ 32 „
Polymerised oil, Stand oil (summer).	4.9% „ 3½ „	8.9% „ 6½ „	9.6% „ 8½ „	10.8% „ 27 „
Boiled oil (containing lead) (summer).	11.8% „ 1 day	14.0% „ 3½ „	12.5% „ 28 „	
Linseed oil heated to 280° C. and 2% Pb. Mn. resinate added.	15.3% „ 5 hrs.	17.4% „ 8½ hrs.	17.4% „ 1 day (film dry)	17.4% „ 5 „
Boiled oil containing lead and manganese (summer).	15.2% „ 16 „	14.6% „ 2½ days	12.8% in 23 days	
Double-boiled oil (summer).	16.1% „ 16 „	14.2% „ 2½ „		
Linseed oil, 2% Lead manganese resinate (no heat) (winter).	14.1% „ 5 „	17.5% „ 8½ „ (film dry)		
Linseed oil blown at 100-140° C., 3 years old (summer).	9% „ 1½ days	15.1% in 2½ „	13.7% „ 4½ „	
Cold blown linseed oil (Calcutta) containing lead (summer).	2.2% „ 1½ „	11.5% „ 5 „	16.7% „ 8 „ (film dry)	
Cold blown linseed oil with 2% Mn. resinate (winter).	12.3% „ 5 hrs.	16.7% „ 8½ hrs.	17.1% in 1 day	17.6% „ 1½ days (film dry)
Blown at 150° C. Linseed oil, 2% Mn. resinate (winter).	14.5% „ 5 „	16.5% „ 8½ „	16.5% „ 1 „	17.5% in 1½ „ (film dry)

boiling process is not always due to the presence of protein and carbohydrate mucilage, but is caused by adulteration with fatty acid glycerides, which polymerise at a temperature of 240°-260° C., yielding insoluble gelatinous products.) When polymerisation sets in, linseed oil is enclosed in the solidifying jelly, but on further heating and stirring the jelly suddenly breaks, and spongy, slimy flakes separate. These flakes harden in the presence of air during the blowing process, and frequently ignite spontaneously, causing explosions and fires; chief among the adulterating oils are Chinese wood oil and candle-nut oil.¹¹

Polymerised Oils (Stand Oil, Lithographic Varnishes).—Linseed oil and drying oils generally thicken on heating at rates depending on the composition of the oil. L. Limis (1835) in Bennebroek, Holland, described a method for the preparation of thickened linseed oil by which the oil was boiled strongly and then allowed to burn, and the flame extinguished when the desired thickening was obtained. Oil thickened by this process was named *Stand*

Oil by Deventer (1868). Andés considers stand oil to be a linseed oil thickened by heat or by superheated steam and a current of air. A. C. Wright¹² states that it is identical with the so-called lithographic varnishes. Extremely thick stand oil is called printers' varnish, but as a painter's material this oil alone finds no application.*

From a summary of the authorities it is advisable to consider stand oil as linseed oil polymerised by heat without driers and without blowing.¹³

In America it is known as lithographic oil. The heating of the oil is performed in a kettle, enamelled or silvered, of aluminium, or copper-bottomed, or even iron alone, depending on the colour desired.¹⁴ If the heating be performed out of contact with the

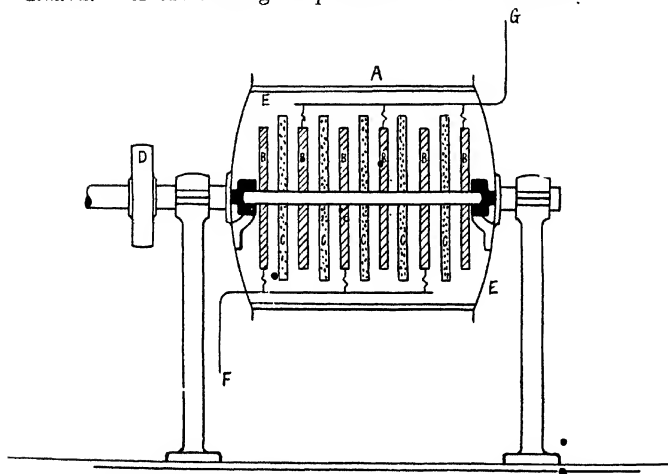


FIG. 14.—Heptinne's process. A, drum; B, metal plates; C, glass plates; D, pulley; E, baffle plates; F and G, electric connections.

air, the kettle is provided with a form of special lid. Otherwise a lid of the usual hood form may be employed connected with a flue or suitable condensing system. The kettle may be heated over a fire or by superheated steam. If iron or copper vessels are employed, the colour will be dark, due to the action of oil on the metals.

When linseed oil is heated out of contact with air, polymerisation ensues.¹⁵ The table on following page shows the changes which Baltic oil undergoes when heated in an atmosphere of carbon dioxide at 250° C.

There is a notable increase in the proportion of solid acids; they are, however, transparent and of gummy consistency. By

* The bodying of linseed oil may be effected by treating with small quantities of sulphur, which element appears to control the degree of polymerisation of a number of drying oils.

	Raw Oil.	12 Hours.	56 Hours.	77 Hours (oil solid).
Sp. gr. 15.5° C.	0.9351	0.9423	0.9664	..
n_D 25° C.	1.4808	1.4835	1.4936	1.4790
Iodine value	196.6	175.2	119.8	..
Oxidised acids per cent . .	0.78	0.29	0.5	3.24
Solid acids *	5.25	7.03	..	48.8
Iodine value of solid acids	17.5	86.4

* Fachini and Dorta's acetone method.

boiling the solid product with amyl alcohol to remove any linoxyn, de Waele obtained an extremely tough insoluble residue, which had an iodine value 94 and was very resistant to the action of alkalis. He considered it to be a closed ring compound (Cyclolin).¹⁵

When other drying or semi-drying oils are heated, thickening occurs at different rates, as shown in the following table :

	Linseed Oil.		China Wood Oil.		Poppy Seed Oil.	
	Raw.	Thickened in CO ₂ at 260° 280° C. 28½ hours.	Raw.	Thickened in CO ₂ at 240° C. 20 minutes.	Raw.	Thickened in CO ₂ at 260° C. 28 hours.
sp. gr. (15° C.)	0.933	0.969	0.9405	0.956	0.9242 (18° C.)	0.9354 (22° C.)
n_D	1.4831 (19° C.)	1.4915 (19° C.)	1.5172 (14° C.)	1.5134 (15° C.)	1.4738 (20° C.)	1.4792 (22° C.)
Molecular weight (in benzol)	805	1680-1701	797	1431	777	900-10
Acidity	0.4	1.7	3.3	2.3	32-33	..
sp. V.	197-203	200-3	192-4	190-201
V. (Wij's)	185	118-34	165-8	143-171	130-6	115-32
Glycerol per cent . . .	9.62	10.4	10.47	8.3
Cryst. hexabromide . .	33.5%	None	None	None
Tetrabromo-acid	50%	6%
Solubility in acetone .	100%	Soluble	100%	Soluble	Completely soluble	Completely soluble
		Insoluble		Insoluble		
sp. gr. (15° C.)	0.9527	0.9763	0.9542 (210° C.)	0.9542 (210° C.)
n_D	1.4846	1.4961
d.W. in benzol	904.75	1788 2517	876
Acidity	7.5	0.2	2.47
V. (Wij's)	92-143	97-121	76-151	93-157

Olive oil and poppy seed oil undergo slight thickening compared with linseed oil, whilst China wood oil can only be heated to 260°C. for twenty minutes without gelatinisation occurring. From the figures given above it is evident that the oleic and linolic acids present in olive and poppy seed oils do not contribute materially to the thickening of linseed oil, the cause of which is due to change in the linolenic acid. It is only when the temperature is raised

to 290° C. that poppy seed oil begins to thicken appreciably. (It must be pointed out that the thickening is retarded by the acidity of the original oil, and the high acidity of the poppy seed oil used may have unduly retarded the polymerisation of the linolic acid. When linseed oil is thickened under the conditions given above, it contains 50 per cent of an oil of high molecular weight, insoluble in acetone. Poppy seed oil thickened at 290° C. contains the same proportion (50 per cent) insoluble in acetone; likewise China wood oil at the point of coagulation shows 50 per cent insoluble in acetone. An examination of the acetone soluble and insoluble portions in the case of linseed oil showed that in addition to polymerisation there was decided indication of changes in the positions of the double linkages of the mixed glycerides of which linseed oil and poppy seed oils are composed.)

The most unsaturated glycerides are polymerised first, but in the case of the isomer of the linolic acid glyceride in China wood oil the polymerisation is extraordinarily rapid, and will be referred to in detail later (page 81). The polymerised molecules are not very firmly held, because on being saponified by sodium methylate at the ordinary temperature they gave a monomolecular methyl ester which polymerised on distillation in a vacuum.¹⁶ In the case of tung oil there was no indication of change in position of the linkages other than polymerisation. The drying power of the thickened oils is reduced, and the viscosity varies according to the conditions of heating. As will be mentioned under China wood oil, polymerisation proceeds rapidly with the formation of stiff gel which is insoluble in petroleum. In linseed oil polymerisation can be carried to the same stage, the change proceeding gradually and being easy to control. This gelatinous product has been referred to on page 54 as cycolin.

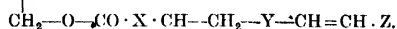
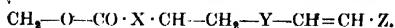
Leeds¹⁷ gives the results of the examination of a number of lithographic varnishes:—

	S.G. at 15° C.	S.V.	I.V.	Oxidised Acids.	Hexabromides.
Raw linseed oil . .	0.9321	194.8	169.0	0.3	24.17
Tint varnish . . .	0.9584	197.5	113.0	1.5	..
Thin varnish . . .	0.9661	196.9	100.0	2.5	2.0
Middle varnish . .	0.9721	197.5	91.0	4.2	..
Strong varnish . .	0.9741	190.9	86.0	6.5	..
Burnt thin varnish *	0.9675	195.5	92.7	0.85	0.0

* Burnt thin varnish is made by heating the oil to its flash point and allowing it to burn quietly with constant stirring.

For further literature on the subject reference may be made to a number of authors given at the end of this chapter.¹⁸

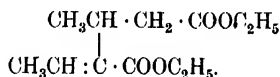
Theories of Polymerisation.—Salway¹⁹ suggested that in the polymerisation by heat the change might be represented by the following scheme:



R = acid radicle of unsaturated oil.

X, Y, and Z represent CH_2 and CH groups respectively in the acid radicle R of the unsaturated oil.

The acid formed is attached to the double linkage in the new diglyceride as in the formation of sulphuric esters of unsaturated acids. Such a compound polymerises according to the scheme given. On saponification a polyglycerine ought to be formed. In the opinion of the writer this could be established if the sodium glyceride produced by the action of sodium methylate on the glyceride were examined, which as yet has not been done. Salway found that the reduction of the iodine value is accelerated by the addition of fatty acids and retarded by the action of glycerine, and that when fats are heated to the polymerisation temperature fatty acids are liberated. The hypothesis is attractive, but further investigation is necessary for its confirmation. Staudinger²⁰ puts forward another type of polymerisation (condensed polymerisation); e.g. crotonic ester $\text{CH}_3\text{CH} : \text{CH} \cdot \text{COOC}_2\text{H}_5$ to crotonic ester :



When the esters of the unsaturated acids from drying oils are distilled, polymerisation ensues, depending on the nature of the ester (cf. Morrell, "On the distillation of methyl elaeostearates"; and Kronstein, "On the distillation of olive oil, arachis oil, cotton seed oil, etc."; also Krafft,²¹ and Bömer and Baumann.²²

If the linseed oil acids be heated at 270°C . in carbon dioxide for six hours, there is a reduction in the acid and iodine values, but not in the case of the saturated palm oil acids. The fatty acids are generally less easily polymerisable than the esters. It has been known for a long time that the thickening of linseed oil is accelerated by alkalis, alkaline earths, or carbonates. Walton, Parnacott, and Taylor used 5 per cent chalk.²³

In commercial samples of calcium linoleate there are found smaller or larger quantities of polymerised oil, and the quantity depends on the amount of lime or the temperature of manufacture. In order to polymerise the fatty acids from the drying oils, or in the manufacture of a thickened oil from the linseed oil acids, it is necessary to add considerable quantities of lime to cause the thickening without loss of material. The presence of small quantities of lime has no deleterious effect on the durability of the oil. Axelrod used metallic chlorides (aluminium chloride) in place of alkaline earths or alkalis, and found that 3 per cent of the chloride gave the

desired viscosity at as low a temperature as 100°-150° C., but the oil must be washed subsequently with water to remove acids and chlorinated bodies, which is not a desirable process.)

Marcusson²⁴ has described a process for thickening oils by silent electric discharge to produce Voltôle (see Fig. 14).

Advantages of Thickened Oils.—The incorporation of thickened linseed and other drying oils into paints and varnishes gives a coating of greater durability and protection against corrosion. Friend, Toch, and Ingle have each published results of exposure tests of paints on iron which undoubtedly support the view.²⁵ The formation of ring complexes consequent on polymerisation or of less unsaturated substances, according to Salway's view, will retard the breaking down of peroxides or oxides of the glycerides on weathering, and will reduce any tendency of peroxide formation extending to other doubly-linked carbon atoms during the drying; this may be observed in the case of China wood oil, which, when unpolymerised, rancidifies with the formation of volatile aldehydes produced by the disruption of a peroxide grouping. The reduction in the water-absorbing power will be referred to in detail subsequently.

It must be mentioned that the amount of polymerised oil present in an oil or varnish mixing must be carefully selected so as not to interfere with the smoothness of working and to prevent drag. Polymerised oil adds to the quantity of thinners required to give suitable viscosity, with the result that evaporation is more rapid on application of the varnish, and often causes shortness.

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CHAPTER IV

EXTRACTION, REFINING, AND BLEACHING OF LINSEED OIL

Distribution and Sources of Linseed.—On the importation of linseed depends the supply of paints and varnishes in the building, engineering, and decorative trades, and for the manufacture of linoleum; during the Great War linseed oil was an important source of glycerine. The following table gives the linseed crop of the most important producing countries: ¹

	1914-18.	1919	1920.
	Tons	Tons.	Tons.
Argentina . . .	668,480	1,067,830	...
British India . . .	467,380	238,770	439,950
U.S.A.	337,420	226,550	272,210
Canada *	193,320	139,010	273,210
Belgium	10,300	22,510
British Isles . . .	12,870	13,940	..
Italy	9,160	11,000	9,000
Egypt	1,450	2,750
Tunis	1,000	1,400	..
Algiers	190	..
Rumania	4,810	4,980	2,700
Bessarabia	2,310	2,550	1,260

* In 1918 the total yield was 200,000 tons as compared with the previous year's average of 350,000 tons a year.

No recent returns are available from Russia.

The oil seed crushing trade is probably one of the oldest industries in the world, and yet it was left for the Great War to bring about full recognition of its vital importance. The major portion of the oil seed crops of the world is produced within the British Empire. The total consumption of oils for industrial and edible purposes in Great Britain is estimated at 600,000 tons annually. No system has been discovered which would enable the whole process of manufacture to be conducted automatically from the cooking kettle to the oil expression, and this is a stage where there is much scope for economy of manufacture. In a well-appointed mill on a pre-war basis the whole operation of receiving, crushing, cooking, pressing, oil filtering, and delivery of produce,

inclusive of interest on capital employed, depreciation, power, labour, consumption of stores, and general working charges, could be carried on for less than £1 per ton, and this upon a raw material whose original average cost would not exceed £12 per ton.

IMPORTS FOR CONSUMPTION OF OIL SEEDS IN 1913

	Linseed.	Soya.	Cotton Seed.
United Kingdom .	654,812 tons	76,452 tons	615,382 tons
U.S.A.	132,357 „	Not separately distinguished	Not separately distinguished
Germany	560,323 met. tons	125,750 met. tons	219,797 met. tons
Netherlands . .	206,035 „ „	27,554 „ „	219,797 „ „
France	237,406 „ „	45 „ „	Not separately distinguished
Belgium	259,105 „ „	Not separately distinguished	Not separately distinguished

1913 was considered as an abnormally high year for linseed.

On conversion of the seed into oil values and deducting the figures for re-export, J. W. Pearson has compiled the following table for 1912-14, 1915, and 1916 :²

	Oil Imports (equivalent of Seed Imports).			Oil Exports.			Oil retained in U.K.		
	1912-1914.	1913.	1916.	1912-1914.	1915.	1916.	1912-1914.	1915.	1916.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
Linseed oil .	158,124	123,554	151,710	27,562	55,927	24,761	130,562	67,627	126,940
Cotton seed oil . .	127,510	117,911	60,212	26,360	36,082	3,397	101,150	81,829	50,815
Fish oil	63,811	91,872	109,061	8,229	4,570	1,146	55,582	87,302	107,915

During the war the demand for oil seeds was increased by three main causes: (1) the demand for glycerine for explosives, which involved "splitting" a quantity of oil far exceeding the normal requirements of the soap trade; (2) the demand for edible oils for margarine; (3) the maintenance of the supplies of feeding cake for cattle. Fortunately the British Empire possessed the very substantial advantage that the supply of oil seeds was amply sufficient for the requirements and left a small margin for export, as shown in the table above. By the system of prohibiting exportation from countries of origin to destinations other than the United Kingdom or the Allies, except under special licence, it was possible to secure in this country any quantities required for which shipping was available.

The largest exporting countries for linseed are the Argentine,

Russia, India, and Canada. The general oil seed production of India is already great, and is capable of further increase.³ The total estimated area (1919-20) under linseed in India was 2,245,000 acres, chiefly in the Central Provinces and Berar (36.2 per cent of the total area under linseed is in British India; the United Provinces account for 28.9 per cent, Behar and Orissa 22 per cent, Bombay 5.2 per cent, and Bengal 5.5 per cent). The Canadian crop is absorbed by the United States, a surplus finding its way to Europe only in bumper years. Although the United States produce nearly 400,000 tons of linseed annually, the full needs of the American seed crushers and paint manufacturers can only be met by large imports in addition.

China is becoming a linseed exporting country. The Soya bean export from China, Manchuria, and Japan is on the decline, having fallen from 400,000 tons in 1919 to a much lower figure. Russia is a great linseed exporting country, from the Baltic provinces as flax seed and from Southern Russia as Steppe seed for cake and oil. Though Russia's annual production of linseed averages over 500,000 tons, her exports in recent years have not averaged more than 150,000 tons a year. For some time to come no large export can be expected from Russia. Small quantities of linseed of the branching variety have been grown in England with satisfactory results.⁴ The variety which succeeds best is the La Plata seed from the Argentine. The seed from the variety grown in England is superior in size, in appearance, and in oil-content to the imported seed from which it was raised; thus 1000 La Plata seeds obtained in 1913 weighed 6.1-6.4 grams with an oil-content of 38.38.4 per cent, while 1000 English-grown seeds from the same variety weighed 7.192 grams with an oil-content of 38.2-42.8 per cent. The yield of linseed oil from seed grown in England does not show a progressive decrease of oil, since successive crops have maintained their high content of oil over a period of three years (1912-15). The yield of seed per acre was 15 cwt., and the oil production, allowing for the manufacture of standard linseed cake, was 35-45 galls. per acre. There is no difficulty in growing linseed; it thrives on moderately good land, the best results being obtained on heavy, loamy soils. It is also specially suitable to be grown in rotation with corn, and does well on recently ploughed land, as it is not attacked by wire-worm. Although the seed is not entirely ripe when carried, it continues to ripen in the "stock," but previous to this the full content of oil has been assured. The ripening is accompanied by a rise in the iodine value (Eyre, private communication). The oil expressed from the seed is equal in quality to Baltic oil, and if the present quality of seed is maintained, British linseed oil will always command a high price in the market.⁵ It can be grown in North Britain (Ife), as well as in the Midlands and the South of England.

The writer has deemed it advisable to make reference to British-grown linseed to show that the country can in case of an emergency produce oil seeds and oil, and the method of cultivation on high-

class land is bound to give better results than the more primitive methods in use in Russia, Argentine, and India.

It must be remembered that the flax or linseed plant (*Linum usitatissimum*) is grown in some countries for fibre only (North Russia, Canada, Belgium, Holland, and Ireland), and the best seed showing the highest percentage of germination is preserved for sowing. It is stated that selected Canadian seed gives a better flax crop in Ireland than Dutch seed. The true flax-bearing plant "Line" has a straight unbranched stem about 40 inches high, consisting of a core, an outer covering, and an intermediate layer of bast tissue. It is the bast tissue which gives the flax fibre, which requires a separation from the core and outer covering by retting and scutching before it can be spun for linen. This variety is not the best for producing cake and oil. The variety grown for seed only (linseed) is branching and shorter in the stem (18-24 inches), and its fibre is of relatively small importance, although it can be retted to produce a coarse, dark-coloured flax which can be spun, but cannot be bleached. The yield of seed per acre from the flax plant is 6-10 cwt., whilst the seed variety (English) gives 10-20 cwt. per acre. The seed from the branching variety is larger, and yields 30-40 per cent of oil. It is from the Baltic Provinces (Riga, Pskoff, and Minsk) that the flax seed is consigned, and after one year's growth in Holland passes to England and Ireland as "Riga-Child Seed"; whereas the seed (Steppe seed) imported from South Russia is crushed for cake and oil. The yield of oil from the different varieties of linseed varies with the locality, but not greatly.

Morocco seed (Mazagan)	41% oil	Plate seed	38-39% oil
Steppe seed	39% "	Dutch (white flowering)	35-55% "
Pskoff	38% "	Indian seed	37-41% "

For fuller information as to the differences between the varieties of linseed, reference may be made to the publications of the British Flax and Hemp Growers' Society, I.-VII.

In the prairie provinces of Canada the flax plant is grown for seed only; in Ontario it is grown for seed and also for fibre. The cultivation of the flax plant in Canada for the production of linseed is as a rule an undertaking distinct from its cultivation for flax fibre. When fibre is to be produced, the seed is sown closely and the stems are pulled out of the ground before the seed is fully ripe. When the seed is required, the sowing is thin in comparison, in order to allow the plants to branch freely, which is undesirable if the fibre is wanted. As free branching leads to the formation of flowers and seed bolls, the harvest yield of seed is obtained from a crop that has stood thinly on the land.

The writer has devoted considerable space to a description of the cultivation of linseed compared with that of flax (line). He has found that there is a common idea that linseed oil is obtained only from the flax-yielding plant. The flax from Canadian linseed, unless the seed is carefully selected, is of inferior quality to that

of the Dutch-Riga varieties. The branching plant is more sturdy, and reference to the cultivation in England of the two varieties will convey a better idea of the conditions under which both may be grown.

Extraction of Linseed Oil from Linseed.—To extract the oil from the seed, hot or cold pressure may be employed; the former is the most common, whilst the latter is only resorted to when a



FIG. 15.—Varieties of flax plants. Left to right: Moroccan, Steppe, La Plata, Dutch.

pale edible oil is required, as in Russia, India, or in parts of Germany. The process is essentially an engineering problem. The broad general methods are two in number; viz. the employment of pressure, or extraction by solvents. It is inadvisable to go into the many details of the plant used, which have been described in many monographs on the subject. The reader who desires to obtain practical information on the subject is referred to a summary of the literature given at the end of this chapter.⁶

A very brief summary of the processes, with diagrammatic representations of the plant employed, must suffice.

If the seeds be small they are crushed in hydraulic presses and the oil forced out of the seed. When the seed or meal is heated during the process of hot crushing, the oil produced is known as hot-pressed or hot-drawn oil; such oil is discoloured by its having dissolved during the expression an excessive amount of colouring matter. The cold-drawing process leaves usually a considerable amount of oil in the cake, but it is freer from impurities, such as mucilage, and is of a better colour. By either hot or cold

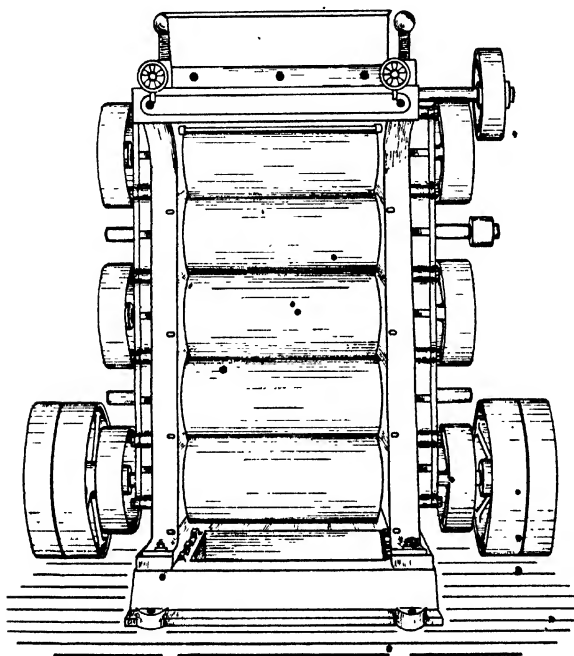


FIG. 16.—Rolls for linseed. (Manlove and Alliott.)

process not more than 90-95 per cent of the total oil is removed from the press cake. The second process extracts all the oil from the seed by use of solvents, benzol, petroleum, carbon disulphide, or carbon tetrachloride. The process in outline consists in allowing the solvent to percolate through the seed or meal in a closed vessel, drawing off the solution and distilling off the solvent.

Anglo-American Crushing System.—Linseed, rape seed, and similar small seeds do not entail preparatory machines to reduce them to a form suitable for treatment in the subsequent recovery process. Such machines are specialised, and are designed to deal

with one particular class of seed or nut; *e.g.* for reducing copra and converting it into meal.

The oil seeds (linseed, rape, etc.) are first drawn through a magnetic separator to remove pieces of metal which may have been added to bring up the weight of the seed, and pass by an endless band conveyor to the crushing mills.

Seed Crushing.—This operation is performed in a crushing mill which consists of five rolls, 16 in. in diameter and 42 in. long,

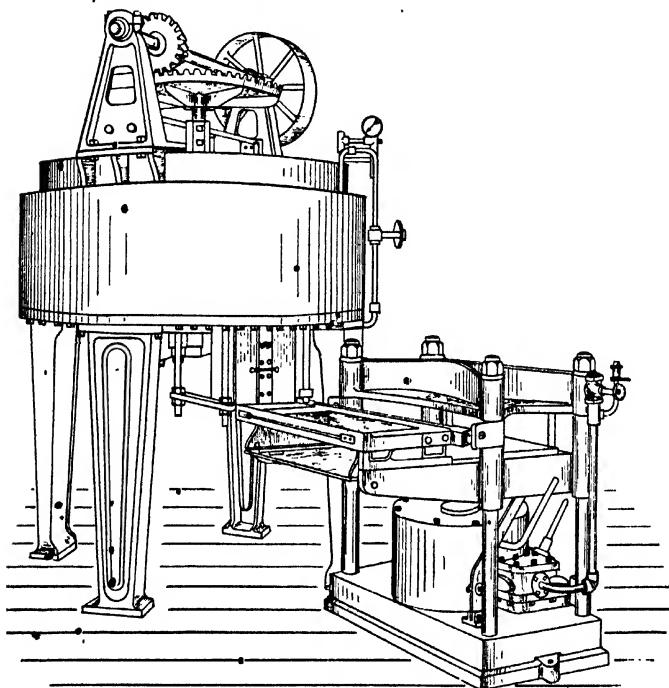


FIG. 17.—Kettle and moulding machine. (Rose, Downs & Thompson, Ltd., Hull.)

stacked vertically, and quite plain on the surface. As a rule they are ground very true and are forced on to their shafts by hydraulic pressure, and thereafter keyed at both ends. The lowest roll is driven at both ends and is provided with two additional pulleys, from which belts are taken to similar-sized pulleys at each end of the third and fifth rolls. The bearings for all the rolls except the lowest are free to slide vertically in their housings, so that the pressure exerted on the seed increases with each step in its descent. The capacity of the rolls is about 15 cwt. per hour.

Heating and Moulding.—The heating of the crushed seed or meal facilitates the expression of the oil, helping to rupture the cells in which the oil is contained; moreover, the viscosity of the oil is reduced so that, on pressing, it flows away more freely. Heating also coagulates the albuminous matter which is retained in the press cake. Frequently a little steam is admitted direct into the kettle, not so much to heat the meal but to improve its condition and to facilitate the flow of the oil; the supply of steam must be carefully regulated, as excess retards the expression of the oil. The time and temperature may be twenty minutes and 170° – 180° F. respectively. The inflow of dry meal and the withdrawal of properly cooked meal forms a continuous process. The meal is immediately rough-moulded in a machine suitable for the press in use, and the slabs are transferred to the press as quickly as they are made.

Pressing.—In the Anglo-American press the space between the ram and the top plate is provided with a number of iron plates (ten to twenty), suspended evenly one over the other. Between the plates are placed cakes of uniform size as they come from the moulding machine. On the application of pressure the plates are forced together, thus squeezing the oil from the meal and causing its exudation through the cloths surrounding each cake. It has been found in practice that the expression of the oil depends more upon the previous preparation of the material than on the actual pressure developed in the press. On the release of the pressure the plates fall again into correct positions. The presses are designed for a pressure of two tons per square inch. The columns are of mild steel, and the press has a large receptacle for the expressed oil, from which the latter is conducted to underground tanks. The plates may be supported by racks, or by links as in the figure. The press is undoubtedly efficient. It is simple and, running in conjunction with the modern meal-moulding machine, is easily and quickly loaded. It is rapidly unloaded, but the stripping of the press-bagging from the cakes may involve considerable labour, so that special machinery may have to be installed for mechanical stripping. The presses are best adapted for dealing with seeds containing a moderate amount of oil. The cake meal

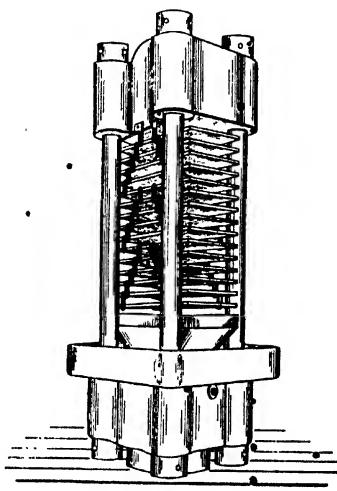


FIG. 18.—Anglo-American press.
(Rose, Downs & Thompson, Ltd., Hull.)

is pressed only on two sides and not around the edges. The plates are often corrugated so as to prevent, as far as possible, the meal from spreading; this is occasionally successful, but not always so, with seeds of a high oil-content. For seeds containing a high percentage of oil a box-cage type of press is preferred which permits of a greater pressure being applied to the meal. The press cakes are the linseed cake of cattle food.

The Solvent Extraction Process.—The 5-10 per cent of oil left in the press cakes is not a loss to the crusher, because the meal from which the oil has been completely extracted is fed direct to cattle without requiring dilution with bran and other material, as is the case with ordinary press cake. Formerly there was difficulty in getting rid entirely of all the traces of the solvent both in the meal residue and in the oil product. The extraction process is in much more general use in Northern Europe than in England, because the farmers there are more accustomed to use feeding-stuffs in the form of meal, while in England linseed cake is generally preferred.

Messrs. G. Scott & Sons, Ltd., London, supply an oil extraction plant in which specially distilled petroleum is used as solvent and the extraction is carried out at 110° C. Benzol was formerly used with satisfactory results, and the extraction performed at the ordinary temperature. Messrs. Scott claim to produce an oil and meal free from solvent and water. It is of great importance to have the meal in a proper condition before being brought in contact with the solvent. In the continuous extraction process the descending stream of oil and solvent from the meal is met by an ascending current of steam, so that petroleum or benzol is carried away with the steam. The working charges are low, although in pre-war days the total manufacturing costs under the extraction process were at least 50 per cent greater than under the hydraulic system, but this statement has been challenged, and the extraction process is now given as 2s. 6d. to 8s. per ton cheaper than the hydraulic. The coal required per ton of raw material with a benzol extraction may be set down as from 2-3 cwt. and the loss of benzol at 1½ galls. per ton of seed treated.

The statement by Mastbaum⁷ that the extracted oil dries slower than the pressed oil must be accepted with reserve. In the pressed oil it was suggested that the more fluid glycerides, *i.e.* the unsaturated glycerides, would be expressed first, but since linseed oil contains mixed glycerides such a differentiation is not possible.

C. F. Eddy⁸ in a summary of progress in the solvent extraction of oils states that in five normal years before the war a solvent extraction plant for flax seed gave a net return of \$1.50 per ton of raw material more than that from a pressing plant.

The use of proper apparatus has greatly reduced, if not eliminated, fire hazards, dangerous poisoning to workmen, and solvent losses. The process which is best for one oil seed is not necessarily the best for another kind. The removal of the last traces of the solvent

by steaming the meal is considered to increase the feeding value of the meal. The expulsion of the solvent from the oil by steam

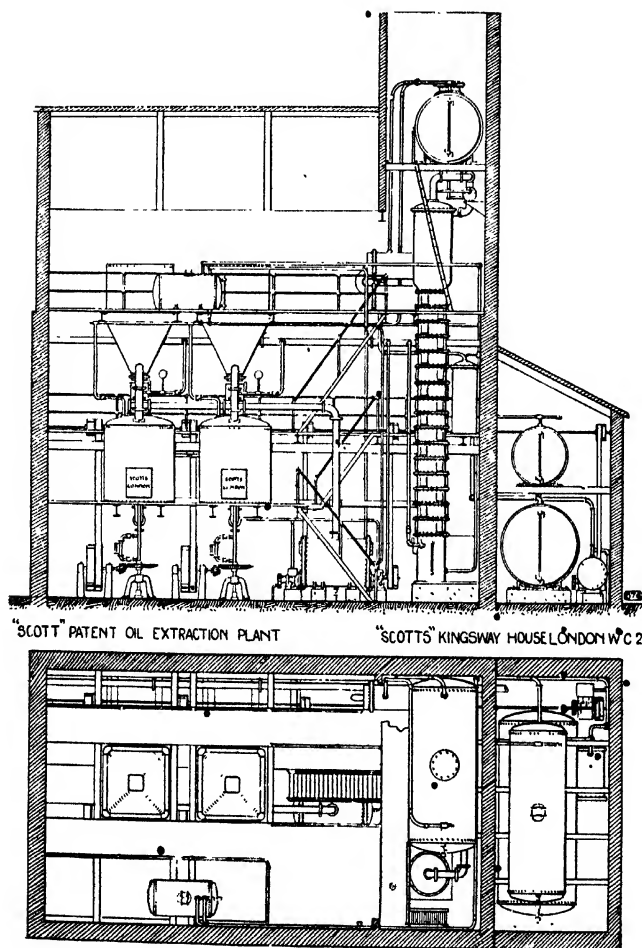


FIG. 10 shows the scheme of an extraction plant designed by Messrs. Scott, suitable for linseed, with a capacity of about 100 tons of seed per week of 140 hours.

is considered by some to destroy the characteristic odour or flavour, leaving a neutral or flat taste. Mashiro Aida⁹ has discovered a test for minute quantities of petroleum spirit in vegetable oils

Refining of oils is said to be simplified by treating them dissolved in the extraction spirit.¹⁰ The writer has observed that the acid value of linseed oil obtained by the extraction process is considerably greater than that of the pressed oil. Eddy concludes that, with improvements constantly being made in processes and apparatus and with the light that is being thrown on the subject by careful study and discussion, the future of the vegetable oil industry lies in the adoption of the extraction process.¹¹

A new process has been patented by Bellwood¹² in which the meal from the crushed seed is subjected to dry heat and no steam is admitted, so that all the water in the material is expelled. At the same time, instead of slow agitation as employed at present, rapid agitation is resorted to and the meal is converted into a semi-fluid, and a large percentage of oil is separated when it is passed into a centrifugal separator of the continuous type, kept at the same temperature as that of the cooking vessel. It is estimated that 50 per cent of the oil is removed by centrifuging, so that a reduction in the usual pressing plant is possible, as also in the cost of bagging before hydraulic pressing; moreover, there will be a reduction in the amount of solvent requisite if the extraction process be used. Where the oil is liable to oxidation, the cooking vessels are covered in and connected with a vacuum pump.

In the case of palm kernels and copra containing 50 per cent and 68 per cent of oil, the centrifuging process removes 38·5 per cent and 50 per cent of oil respectively. The success of the method depends on complete elimination of water from the meal, because a small amount of moisture causes the semi-fluid mass to solidify immediately. The difficulty to be overcome in the process is that of designing a centrifuge which will work continuously on different kinds of material.

Refining of Linseed Oil.—Linseed oil after extraction from the "meats" in the pressing process contains foreign matter called "foots" derived from the seed. The more unripe and the damper the seed the greater is the quantity of the foots. They are removable by settling, filtration or centrifuging, but the separation is slow and the oil is improved by tanking, even after careful filtration. The foots are partly albuminous and partly of a carbohydrate nature. The former elements are generally removed in the first stages of tanking and filtration, whereas the latter require a heat or special treatment for their separation. The water in the oil derived from the steaming of the linseed meal during the crushing separates out on tanking incompletely, because some is retained by albuminous and carbohydrate mucilage, which is itself soluble in water. When linseed oil is heated rapidly to 260° C. (500° F.) the moisture is expelled and the mucilage of carbohydrate character separates as gelatinous "spawn," or the oil "breaks." The oil may sometimes be darkened owing to charring of the mucilage. Generally the colour is improved if a well-matured oil is heated, as the mucilage in its gelatinisation extracts much of the colouring matter. The quantity of mucilage

varies with the nature of the oil and with its age. Young and damp oil gives more mucilage on heating, since the tanking assists its deposition. If linseed oil be heated slowly up to 500° F., the separation of the mucilage is retarded, possibly due to increasing viscosity of the oil during the slow heating; on the other hand, if the oil be allowed to cool very slowly, part of the coagulated mucilage redissolves or cannot be separated by centrifuging.*

Mucilage.—The foots which separate out on heating contain 91.4 per cent oil and 8.6 per cent dry mucilage. Thompson¹³ found that a sample of freshly expressed oil heated to 400° F. gave 0.277 per cent deposit; this figure is misleading as to the real amount of mucilage present, since much depends on the condition of heating. The writer finds that in testing linseed oil by the breaking test, if the oil be heated to 260° C. in a test tube, allowing a rise of 50° C. per minute and centrifuging one hour after heating while the oil is still warm, the percentage of mucilage in the case of a good oil may vary from 3.6 per cent to 4.6 per cent by volume. If the oil be allowed to stand overnight before centrifuging, the amount will fall to 0.3 per cent or even to nothing, showing that either the mucilage had dissolved again partly in the oil on cooling, or that its degree of dispersion had been modified. Thompson found that the mucilage (0.277 per cent of the oil) contained 47.79 per cent ash (0.117 per cent of the original oil), consisting of 20.96 per cent CaO, 18.54 per cent MgO, and 59.85 per cent P₂O₅. Ingle gives to the mucilage a content of 14.9 per cent ash, of which 2.7 per cent consisted of phosphates (P₂O₅). The composition of the mucilage must depend on whether the oil has undergone a preliminary refining process previous to despatch to the user, or whether both albuminous and carbohydrate mucilage are present. The writer has found alumina and silicates in the ash obtained from the spawn of commercial linseed oils. The statement that oxidation of the mucilage occurs before that of the oil requires confirmation, as well as the statement that the fish-like smell of certain linseed oils is due to the oxidation of the lecithin present in the albuminous matter in the oil. Thompson found that the spawn contained less than 1 per cent nitrogen, and owing to the large amount of bases present he does not consider the assumption of the presence of albuminoids to be in accordance with the facts, or that the phosphorus present can be due to lecithin. In the writer's experience linseed oil of good quality as supplied from the seed crushers contains no nitrogenous mucilage.

The nature of the non-nitrogenous "hops" is indicated by Hilger,¹⁴ who obtained a water-soluble mucilage, reacting acid, of a carbohydrate nature, to which he ascribed the formula (C₆H₁₀O₅)₂ (C₆H₈O₄)₂, or a galactose and pentosane substance, from which dextrose, galactose, arabinose, and xylose were obtained. The mucilage contained calcium, magnesium, iron carbonates, and phosphates in considerable quantity.

* The effect of storage on drying oils is to cause a slight increase in the specific gravity and acidity of the oils (Circ. 60, *Paint Mfrs. Assoc.*).

Neville¹⁵ has investigated the ash from the water-soluble mucilage of linseed. It was extracted from the seed by cold water and its content was 6.28 per cent of the seed treated. If the extraction be performed by 1 per cent sulphuric acid, the amount of proteid matter obtained is greater, whereas water extraction yields a solution which gives only a slight precipitate with phosphotungstic acid reagent. The carbohydrate precipitated by alcohol from aqueous solution is insoluble in all organic solvents. The aqueous solution gives gelatinous precipitates with salts of heavy metals. Neville considers that this water-soluble mucilage is well described by the term muco-cellulose of Cross and Bevan, being a carbohydrate showing all the characteristics of hydrated cellulose. Like Hilger, he was able to isolate derivatives of the galactose, pentosane sugars. The presence of mucilage in linseed oil is a factor which is often overlooked. The actual weight is minute, but its oil absorption is very high, as well as its power to absorb water. Its properties in solution in oil are comparable with those of gum-arabic in water. This absorptive power for the medium and for the substances dissolved or contained therein has its advantages and disadvantages. Suspended material settles slower and the presence of water, held by the mucilage, has an emulsifying action which retards or may prevent the brightening of a mixing. Its effect on the drying power may be detrimental by reason of the nature of the mucilage, but at the same time it may act, as in the case of gum-arabic, as a protective colloid for metallic driers and so be a promoter. Generally its presence may be considered as detrimental to good drying, due mainly to its water-absorbing powers.

There are several methods which may be used by a varnish maker to remove mucilage from oil. One is by filtration of the oil through fullers' earth, or by agitating therewith and allowing the oil to clarify on standing. The removal of the mucilage by breaking the oil at 260° C. is only possible when centrifugal plant is employed, because filtration of the separated mucilage is too difficult. Other substances have the same power as fullers' earth, viz. borax, fused sodium carbonate, slaked lime, magnesium oxide, litharge, and zinc chloride (the oil requires subsequent washing to remove the hydrochloric acid formed), dried white copperas ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$), zinc resinate, calcium resinate, and calcium carbide. Taine and Hauff¹⁶ recommend a trace of slaked lime to be used. Charles de la Roche claims for calcium carbide. M. Ekenborg¹⁷ removes mucilage by heating the oil with glycerine and alkali hydroxide at 100° C. and above, whereby a neutral soap separates. For further information and full details as to the refining of oils reference may be made to Lewkowitsch (*loc. cit.*) and Chalmers (*loc. cit.*). The following details will give an idea as to the practicability of two of the methods :

180 gallons of linseed oil were churned for nine hours with 90 lb. of dried fullers' earth (it is advisable to dry the earth before using because it is more efficient in that condition). After

one month's settling the oil was drawn off and subjected to a breaking heat test. No mucilage separated.

162 gallons of linseed oil were mixed with 18 gallons of linseed oil in which 10 lb. of zinc resinate had been dissolved. After a month the oil was drawn off, leaving 5 gallons of cloudy residue. On testing for mucilage by heating to 260° C. nothing separated, but there was a slight darkening of the oil.

The writer maintains that it is possible to prevent the breaking of oil on heating and to remove the mucilage by churning with solutions of certain salts. The concentration of the salt must be considered and must not exceed 10 per cent. Ten per cent solutions of sodium chloride and aluminium sulphate are most suitable. Sulphuric acid (1 in 10) can also be used. Ten per cent ammonium alum or 10 per cent aluminium sulphate cause a coagulation of the mucilage so that the oil does not brighten easily. It is advisable to give a treatment with a second quantity of the salt solution, so as to ensure the complete separation of the foots. It is unnecessary to give the oil a washing with water, and it is inadvisable to do so because of persistent cloudiness.

It must be pointed out that some of the processes suggested are essentially moisture-removing, *e.g.* sulphuric acid, calcium carbide, and white copperas (ZnSO_4 , H_2O); some in which the adsorptive power of the substance added is the active factor, *e.g.* fullers' earth, which in addition to removal of mucilage exercises a decided bleaching action; others, *e.g.* action of lime and calcium and zinc resinsates, probably act in preventing the breaking by virtue of their specifically alkaline or acid reactions. The action of dilute solutions of salt and ammonium sulphate are probably methods by which the carbohydrate mucilage is actually dissolved out of the oil. It is doubtful whether the mucilage is completely removed by any of the processes mentioned. Generally the treatment of the oil by any of the special chemical methods is not encouraged, because of their expense, and tanking or treatment with fullers' earth is on the whole preferable. In many varnishes the presence of mucilage is not noticeable, but in special mixings it exercises, as indicated on the previous page, deleterious effects in retarding the settling of driers, softening the film, and in absorption of moisture during drying in the air.

Bleaching of Linseed Oil.—The paler the linseed oil the paler the varnish obtained, so that the importance of processes to give a colourless oil without damaging its properties is great.

(a) *Fullers' Earth Method.*—This method is extensively employed in England, America, and Germany. It is advisable to dry the earth before adding it to the heated oil. The oil is allowed to settle, and is then filtered. It is possible to regenerate the spent fullers' earth by extraction of the oil by a volatile solvent and heating to 400° C. to expel water and solvent. The activity is only slightly reduced by the regeneration process. Generally the amount of earth used is carefully controlled, so as to avoid

unnecessary regeneration of spent earth. Fullers' earth (magnesium aluminium hydrosilicate), although valuable for bleaching vegetable oils, is of little value for mineral oils. Deposits have been found of an aluminium hydrosilicate which possesses a bleaching power superior to fullers' earth.¹⁸ It is stated to absorb 45 per cent to 60 per cent of its weight of oil, whilst fullers' earth, ferrocyanide residues and decolorising carbon powder, absorb 100 per cent to 200 per cent. Oils bleached by this earth darken less on heating than oils bleached by fullers' earth. If a preparatory sulphuric acid treatment is employed, it is necessary to remove the excess of acid before bleaching with the aluminium hydrosilicate, otherwise the action is completely inhibited. The addition of a certain quantity of the prepared German earth to neutralise the excess of acid previous to the addition of the main quantity is necessary. The earths Frankonite, Siltonite, and Tonsil are the most efficient. With linseed oil 5 per cent to 10 per cent Siltonite (F. and S.) will give an almost water-white product. The oil is heated to 80° C. and then agitated for forty minutes with the bleaching earth. It is claimed that light mineral oils (s.g. 0.850) of a yellow colour can be bleached in thirty to forty minutes by 3 per cent to 5 per cent of the bleaching earths at a temperature of 80° C. Similarly heavy machine oils can be bleached to a straw colour by 5 per cent to 10 per cent of the earth at 120° C.

The fullers' earth process gives the finest and palest varnish or artists' oil.

(b) *Sulphuric Acid Method*.—One per cent sulphuric acid of 66 Bé. is added to the oil slowly with agitation. After agitation for a sufficient time, the mixture is allowed to settle overnight; the clear oil is then drawn off, agitated with water, and finally with steam. After settling, the washing is repeated. Such oil contains a little free fatty acid. The strength of the sulphuric acid may be reduced to 15 per cent.

(c) *Caustic Soda Method*.—Linseed oil is agitated with 3½ per cent of its weight of a 15 Bé. solution of caustic soda for about half an hour or more. The mixture is then heated to 100° F. and cooled to 70° F., allowed to settle, and the clear part drawn or siphoned off, whilst the residue is filtered. To the clear oil 7 to 8 per cent of its weight of fullers' earth (dried) is added and the temperature raised to 150°-180° F. with constant agitation. After half an hour's agitation at that temperature the bleaching is complete and the oil is filtered.

This process makes a very pale oil, and if afterwards sun-bleached it yields the palest linseed oil obtainable. Sun-bleaching makes little or no difference in the colour of varnishes made from the oil, because on heating it suffers a darkening to give products of the same colour as if the sun-bleaching had been omitted.

(d) *Bichromate Method*.—A German process for oil to be used for amber varnishes is described by Sabin (p. 41). 1000 lb. of linseed oil previously heated to 100° F. is treated slowly with a bleaching solution made from 12½ lb. of sodium or potassium

bichromate dissolved in 60 lb. of water to which 3½ lb. of manganese dioxide have been added, and while hot 30 lb. of hydrochloric acid are poured in. The mixture is agitated for half an hour or longer and allowed to stand five days (summer) or ten days (winter). The clear oil is drawn off and tanked for two months (summer) or four months (winter).

The above is an instance of many chemical processes which have been proposed; *e.g.* bleaching by use of: MnO_2 and HCl ; KMnO_4 and HCl ; $\text{K}_2\text{Cr}_2\text{O}_7$ and HCl (all these give chlorine); super-oxides and dilute H_2SO_4 ; calcium carbide, oxygen and ozone. The last is becoming more popular in view of improvements in the ozonised air plants.

Bleaching with Ozonised Air.—Linseed oil may be bleached by ozonised air to an almost colourless oil. The general type of tube employed in the construction of these ozonators is illustrated in Fig. 20. Alternating electric current for the operation of this machine is first led to a transformer where it is stepped up to a potential of about 10,000 to 12,000 volts. One of the transformer leads is then brought to the busbar of the machine and the other to the frame, so that a complete circuit may be traced from the transformers through the inner cylinder, across the air-gap and through the glass tube, which forms the dielectric, to the copper plating on the outside of the glass tube, which in turn is grounded to the frame and then back through return leads. As the high-voltage current passes through the air-gap, it does so in the form of brush discharge which forms a purple ring completely filling the annular opening. This is not a spark, but a true so-called "silent discharge," although as a matter of fact it is accompanied by a rushing sound. The copper tube which is shown surrounding the glass tube is employed for the protection of the glass, and while entirely non-essential as far as the operation of the machine is concerned, it is of great practical importance, preventing the frequent breakages and shut-downs which would occur in cases where the glass surfaces were left exposed. The water shown surrounding the tubes is employed to keep down the temperature, which becomes high when the machine is working. In this type of ozonator the generating tubes are mounted in a casing so formed as to provide a chamber at each end of the open tube. Air is admitted, under light pressure or subject to suction, into the chambers at one end of the tube, and passes through the brush discharge and the annular space between the inner and the outer electrodes. A portion of the oxygen of the air is ozonised and the ozonised air is conducted through piping to the point of application. All the air going into the generating chamber is passed through trays with bottoms of wire gauze filled with a layer of calcium chloride, so as to dry the air and ensure successful operation of the ozonators. The actual amount of ozone which can be generated in a tube of this kind is nearly proportional to two factors—namely, the voltage and the frequency of the electric current forming the discharge. The practical limit of voltage has been found to be from 10,000 to

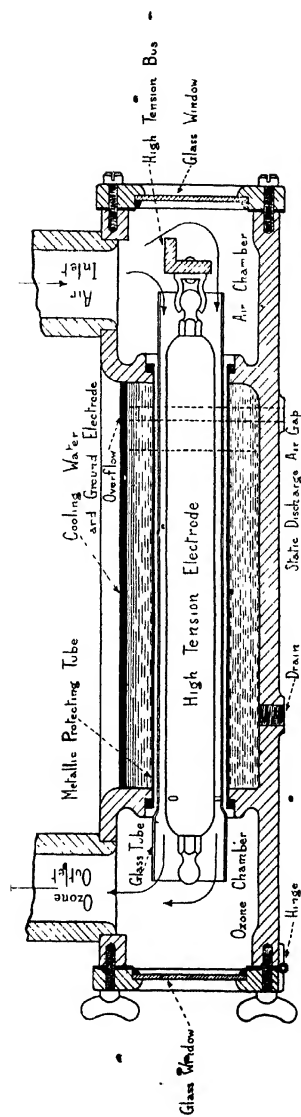


FIG. 20.—Sectional view of industrial ozonator tube.

12,000 volts, the limitation being caused by the difficulty of securing adequate insulation when this is exceeded. Most of the small outfits are operated at a frequency of 60 cycles. On medium-sized plants 133 cycles is often used, thus securing the double output from each tube. Up to now the highest frequency found in practical use in the largest installations is 500 cycles. For treatment of linseed and similar oils for bleaching, bodying, and solidifying, the oil should be treated in a mixer in which it is continually agitated by revolving paddles. Bubbling ozone through the oil is unsatisfactory and requires much longer time for results. Rapidity of thickening depends on the temperature at which the oil is treated. Raw oil treated at 65°-90° C. thickens rapidly, but the oil becomes darkened. When run at temperature below 40° C. the thickening proceeds more slowly and eight to ten hours are required for solidification, but the oil is bleached. For bodying paint or varnish a treatment of six hours is usually sufficient. For linoleum the average treatment is eight to ten hours.¹⁹ After treatment with ozonised air (Ozonair plant) for twenty-four hours a sample of oil, to which a trace of manganese drier had been previously added, was almost colourless and gave the following constants compared with those of linseed oil :

	S.G.	Viscosity. [Glycerine-100]	I.V.	Acid Value.	Drying Time.
Unbleached linseed oil	0.9320	6.88	183.5	0.975	Wet in 6 days
Almost colourless ozonised oil	0.9470	10.35	170	3.8	Dry in 6 days

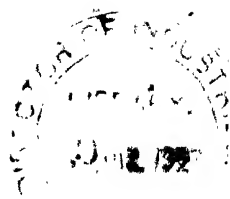
It is evident that specific gravity, acidity, and viscosity have all risen, but the iodine value has fallen slightly although the drying time has improved, as is the case with boiled oil. This method is more promising than where the bleaching is effected by addition of chemicals. Reference may be made to the many patents described in the *Journal of the Society of Chemical Industry* under the heading of the Bleaching of Oils.

The following notes show the effect of ozone treatment on various oils, fats, and waxes (Ozonair, Limited) : Tung oil is easily thickened, but the investigation as to bleaching or deodorising is not complete ; cotton seed oil bleaches fairly easily according to grade and quality, but requires subsequent treatment for deodorisation and improvement of flavour. Olive oil bleaches very easily, the darkest varieties known as " Sulphur " are bleached to the ordinary olive colour ; poppy seed oil can be bleached without thickening, or bleached and thickened to a syrup. It thickens less readily than linseed. For edible purposes it requires subsequent treatment. Soya oil is bleached fairly easily according to grade and quality, but requires subsequent treatment for deodorisation. Lanoline is easily

bleached, but Carnauba and Montana waxes are not. Beeswax may be successfully bleached, but only in the case of the darker varieties.

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CHAPTER V

OTHER DRYING AND SEMI-DRYING OILS

THE gloss and durability of linseed oil films are much improved by admixture with its polymerised forms. Coatings of resin and linseed oil are moisture-absorbing, even after the unsaturated glycerides have been apparently transformed into linoxyn, and after a time show on exposure a poorness of lustre and a tendency to fine cracking which is dependent on the resin content. The durability of the polymerised linseed oils neutralises this failing only partially, and it is becoming more and more the custom to incorporate with linseed oil other drying oils, especially those which are easily polymerisable and of greater rapidity of drying, whereby the linoxyn content is rapidly increased so that it may provide a film resistant to the weather. The chief of these oils is China wood oil, which gives a tough film of high gloss and allows of the use of rosin, instead of copal resin, provided that proper precautions as to mixing and concentration are taken.

CHINA WOOD OIL (TUNG OIL)

China wood oil is extracted from the nuts of several varieties of *Aleurites*, of which *Fordii* and *cordata* are the most important. The pod or nut is of apple-green colour about the size of a small orange, and contains usually three or five seeds resembling shelled Brazil nuts, but much smaller. The oil from *Aleurites Fordii* is identical in chemical composition with that obtained from *Aleurites cordata*. The Tung-yu-shu (Tung oil tree),* *Aleurites Fordii*, is indigenous to Central China throughout the Yangtse Valley from Ichang westwards to Chungking. In the wild state the tree seldom grows more than 15 ft. with a spread of 12-18 ft., producing on maturity an average of three hundred fruits annually of from fifteen to eighteen to the lb. when dried. The tree is highly ornamental in foliage and flowers, suggestive of possibilities for shade-tree purposes. When cultivated the trees will reach a height of from 20 to 25 ft., with a spread of 30 ft., and after eight to

* *Aleurites montana* (Mu-yu-shu, wood oil tree) has a hard and woody ripe fruit, hence the name wood oil tree. The name Tung is applied to several widely distinct trees having large heart-shaped leaves; among them is *Paulownia*, of which four or five species occur.

ten years will produce an average of a thousand fruits annually. In very wet years and in favourable localities the proportion of female to male flowers will be one female to five or seven males; in dry years as few as one female to twelve to fourteen males. It is essentially a hillside tree, thriving in the most rocky situations and on the poorest of soils, where there is a minimum of 29 in. of rainfall. It will stand drought as well as a few degrees of frost, but the young fruit is very sensitive to frost, which often destroys or malforms them.¹ In S.W. China, extending to Thibet, the preponderating species seems to be *Al. cordata*, differing but little from *Al. Fordii*. In S.E. China *Al. triloba* and hybrids of the species with *cordata* and *Fordii* are plentiful. In the Philippines *Aleurites moluccana* and *trisperma* (Lumbang oil) are found. A new variety lately discovered in S. China having more females than males has been grafted on *Al. Fordii* with success. In Japan *Al. vernicia* (*A. cordata*) alone seems to thrive (see Japanese wood oil). The seeds of *Al. Fordii* are treated by crude native methods and the yield is 40 per cent from an oil-content of 52 per cent (the average yield from the whole fruit is 17 per cent). The Chinese method of extraction is of interest. The fruit is gathered and piled in stacks, covered with straw or wet grass and allowed to ferment until the flesh is easily removed. The partly decomposed husk is used as a fertiliser. The oil extracted from the seeds is pale in colour, but the moisture content and acidity are high. In other districts the husk is removed by roasting the fruit in shallow iron pans until it bursts, when the nuts are separated by hand. The dry husks are used as fuel and the ash sold to the native potash maker, who extracts the potash by crude methods. The oil obtained by this method is darker in colour, particularly if too great heat has been employed in the roasting. In either case the final treatment is the same, viz.: the nuts are ground to a coarse meal in a crude stone mill worked by buffalo power. The meal is roasted slightly and then steamed by being placed in wicker baskets suspended over boiling water. It is then placed in vats and allowed to drain. The meal is prepared for the presses by placing it in crude iron frames with straw packing outside. About sixty of these frames are stacked in antiquated wedge presses, and pressure applied by a system of driving in wedges. The oil drains out through the straw and drops into a pan at the bottom of the press. The oil is prepared for shipment by being run into wicker baskets lined with varnished paper, and shipped to Hankow. The crude oil is refined by the merchants, who run it into vats, heated by steam coils to expel as much moisture as possible. After being pumped into settling tanks so as to remove refuse, the clean oil is drawn off from the top; this constitutes the "f.a.q." of commerce. The refuse is returned to the dealers, who sell it to the natives to be mixed with gypsum for caulking junks and sampans. The worst part of the refuse is burnt for Chinese ink.

Aleurites montana from Mu-yu-shu (wood oil tree) is common in the regions around Wuchow to the west of Canton, whence

it is exported to Hongkong. The oil cake is poisonous and can only be used as a fertiliser. The blending of the oils from different varieties of *Aleurites* is common, as well as of different grades, and leads to complications which may be illustrated as follows :

	I.V.	Colour.	Specific Gravity.	Gelatinisation.
<i>Aleurites Fordii</i>	173	Amber	0.942	Complete on heating
<i>Aleurites triloba</i>	140	Almost white	0.925	Very slight gelatinisation

Buyers must safeguard themselves against adulterated oil, as it is a common practice for the natives to mix in cheaper native bean oil. *Aleurites triloba* mixed with perilla oil gives an emulsion of great excellence and paleness, which is claimed to be superior to those produced from linseed oil.

Hankow is the chief port of export and 80 per cent of the oil is shipped therefrom. A little goes through South China to Hongkong, but this is not held in such high repute.

Japanese wood oil (*Elaeococca vernicia* or *Aleurites cordata*, R.Br.) is of less value than China wood oil from *Aleurites montana* and still less than the oil from *Aleurites Fordii*.² It is similar to tung oil, but gelatinises less readily.

Aleurites cordata from the Fukui province of Japan gives fruit consisting of shells, 37 per cent, and kernels, 63 per cent, containing 51 per cent of light golden yellow oil, which possesses the following constants : I.V. 150.2 (Wijs) ; 154.2 (Hübl) ; Sap.V. 193.2 ; Acid Value, 0.9 ; Sp. Gravity (15.5° C.), 0.9342 ; $n_D^{25^\circ C.}$ 1.4981. The oil can be used to a considerable extent for the same purposes as China wood oil.³

Tung oil has the following uses in China :

- (1) As a paint oil for outside work.
- (2) The cruder grades of oil are used on native boats as a paint, varnish, and preservative, all in one.
- (3) With the addition of the mineral substances "t'u-tsz" and "t'o-shen-shin" it serves as a waterproofing varnish for silks.
- (4) As an adulterant of lacquer varnish.
- (5) As an illuminant.
- (6) When mixed with lime and bamboo shavings it is used for caulking native boats.
- (7) The soot from burnt wood oil produces the best quality Chinese ink.
- (8) As a dressing for leather and a varnish for furniture!

Recently the cultivation of *Aleurites Fordii* has been undertaken in the Southern States of North America. In 1914 forty thousand trees were in cultivation and the results were satisfactory. Cultivation experiments are being conducted in India (Raw Materials Committee, Imperial Institute, 1920). Possibly the trouble respecting

the unsuitability of the cake as a cattle food will be overcome, and the application of modern methods of crushing and refining on the spot will stimulate the cultivation of *Aleurites*. The development of the extraction method for obtaining oil from seeds, together with suitable previous preparation, will give much larger yields of extracted oil than is provided by the crude native treatment. In 1906 the export from Hankow was nearly 29,000 tons, and the amount does not seem to have increased as much as would be expected, as shown by the export figures for 1914-19:

1914. 26,300 tons.	1916. 39,000 tons.	1918. 29,300 tons.
1915. 18,100 „	1917. 24,100 „	1919. 36,500 „

It must be remembered that the conditions are different now. Between 61 and 79 per cent of the export goes to the U.S.A. The literature on tung oil is very extensive (*Index to Patents, Technology and Bibliography of China Wood Oil*, A. H. Stevens and J. W. Armitage).

Tung oil has marked peculiarities differing from linseed oil in the following respects: it dries in about two-thirds of the time of linseed oil, giving a film which is white, dull and opaque, and crinkled. These effects are much reduced in the presence of driers, but they are especially marked if the drying be retarded in a gas-laden or foul atmosphere. The surface puckers or webs and becomes matt with a finely-radiating crystalline appearance. Often the film becomes uniformly opaque like ground glass. If the drying be performed at temperatures above 80° C. in a good draught the film is transparent and smooth. The webbing and fine cracking are due to unequal volume changes in the film on surface drying. The matt surface may be due to the formation of the solid isomer; such an isomer is produced when wood oil is exposed to light. The crystalline stereoisomer, a monomolecular glyceride of β -elæostearic acid, is rapidly oxidised to an amorphous white peroxide.⁴ Another peculiarity is the rapid gelatinisation of the oil. When heated to 282° C. for nine minutes (Browne's heat test) it sets to a hard transparent jelly. This property is used for the detection of impurities in the oil, and it is stated that the addition of 5 per cent of another oil, e.g. soya-bean oil, will retard the gelatinisation at the above temperature.⁵ The gelatinisation is due to polymerisation, which differs greatly in rate from that of linseed oil. In Circulars 84 and 100 of the Educational Bureau, Paint Manufacturers' Association of U.S.A., are given the standards for tung oil as settled by the American Society for Testing Materials.

The table on following page shows a comparison of the constants of linseed and China wood oils.

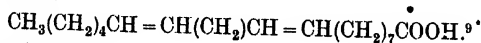
E. Ware⁶ states that the detection of adulterants in China wood oil may be based on differences in optical dispersion.

The preparation of the metallic salts derived from the oil has been referred to in Chapter II. p. 39. Boiled with caustic alkalies it yields soaps which are granular in comparison with those of linseed oil. The alkali salts of α - and β -elæostearic acid ($C_{18}H_{32}O_2$).

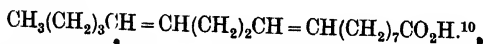
	Linseed Oil.	Tung Oil.	American Standards.
Specific gravity (15° C.) . .	0.933	0.9405-0.942	min. max. 0.939-0.943
n_D	1.4831	1.5174 (12° C.) 1.475 (40° C.)	1.515-1.520 (28° C.)
Acidity	4.6 as oleic acid	3.3	6% as oleic acid
Saponification value	197	192	190-195
I. Value	185 (Wij's)	168 (Wij's)	165 (Hilbl)
Percentage increase in weight on exposure to air	17.6 (8½ days)	13.5 (8½ days)	..
Heating gelatinisation test at • 292° C.	Several days		12 minutes

of which the two varieties of tung oil are the glycerides, are crystalline substances, which are sparingly soluble in water, especially the β -salt. Owing to the limited variety of components China wood oil lends itself readily to favourable investigation. The only other component of the oil, except the β -glyceride, is olein to the amount of 10 to 15 per cent (Fahrion states that 2 to 3 per cent solid acids are present, and M. Nonaka⁷ states that 2.5 per cent stearic acid is present). It gives no ether-insoluble bromide either as glyceride or when transformed into the corresponding acid. A solid tetrabromide of the same melting point has been obtained from the α - and β -acids, which is isomeric with the tetrabromide of linolic acid.⁸ The peculiar drying properties of tung oil must be connected with the orientation of the double linkages in the molecule, since it is isomeric with the glyceride of linolic acid (a much slower drying oil), which is present in poppy seed oil to the extent of 65 per cent.

Linolic acid :



Elæostearic acid :



The most important property of tung oil is its rapid polymerisation on being heated. Schumann¹¹ has put forward the view that a dipolymeride or dimeride is first formed which afterwards gels. He discusses the methods of preventing coagulation, which is a most undesirable property, although the rapid formation of the dimeride is of great importance and its proper control has been the subject of much investigation. Careful research is overcoming the difficulties due to rapid gelatinisation. The coagulation appears to be governed, among other factors, by the acidity of the system and to some extent follows the course of linseed oil thickening, but at a far more rapid rate. The addition of basic substances facilitates the formation of the polymeride, although, when present in sufficient quantities to form a high percentage of soap, the gelatinisation is retarded, whereas the presence of acid by-products of the oil or of acidic resins, e.g. rosin, retards the formation of both the polymeride and its coagulated form.

Krumbhaar¹² has studied the effect of heat on China wood oil in carbon dioxide steam between 200° and 300° C. The iodine value, after four hours' heating at 200° C., fell from 160.3-134.5, while the saponification value was practically unchanged, 193.2-190.1. (He concludes that differences of polymerisation of wood oil and linseed oil are of degree only.)

When tung oil is heated to 240° C. for twenty minutes and the heating stopped as soon as any substance insoluble in light petroleum is formed, in other words as soon as gelatinisation begins, the constants of the oil compared with those of linseed oil are as shown on p. 54.

The polymerisation of wood oil may proceed on the lines indicated by Salway and Morrell,¹³ provided the acid material present is in sufficient initial concentration to prevent the formation of the direct polymeride and to allow of the production of the less saturated glyceryl-polymeride at a temperature much above the ordinary gelatinisation point of China wood oil. Such a transformation produces another modification of wood oil.

Morrell¹⁴ and Schapring¹⁵ have observed that the refractive index of tung oil diminishes when the oil is heated. The high value (1.5192 at 15° C.) of the refractive index is useful in the detection of impurities in the oil, which invariably possess lower refractive indices.¹⁶

The methods of treatment of tung oil in varnish mixings are essentially trade secrets. When the defects of coagulation and webbing of the varnish film are overcome by the varnish maker he can produce a much improved protective coating, but skill and judgement are necessary in the treatment of the oil. Owing to the rapidity of coagulation of the oil it is very difficult to incorporate it with copal resins. The published practical methods for the treatment of wood oil will be discussed under Tung Oil Varnishes (p. 247), where it will be shown that its great importance lies in the hardness, elasticity, and high water-resisting power of the films, whereby rosin may be used instead of copal resins to impart the requisite lustre and hardness.

When China wood oil is saponified it gives a white crystalline acid (α -elaeostearic acid), m.p. 41° C., which is easily oxidised in the air. The solid modification of tung oil (m.p. 61°-68° C.) is very rapidly oxidised to a white amorphous solid. The crystalline glyceride on saponification and subsequent decomposition of the sparingly soluble crystalline alkali soap yields β -elaeostearic acid (m.p. 72° C.). The methyl ester of α -elaeostearic acid is converted (85 per cent) on distillation in a vacuum into β -ester. The ethyl β -elaeostearic ester is partially polymerised by distillation *in vacuo*.¹⁷ On exposure to air at the ordinary temperature it gains 10.24 per cent in weight in twenty-four hours with a maximum of 12 per cent, which finally remains constant at 11.1 per cent; $C_{20}H_{38}O_2 + O_2$ requires 10.39 per cent.

The oxidised oil reduces Fehling's solution slightly, and on treatment with Schiff's reagent for aldehydes it becomes purple in

colour. When warmed with pure potassium iodide no iodine is liberated, until a few drops of dilute sulphuric acid are added. The ethyl ester on exposure to air does not set, and remains quite clear; there is no matt surface as in the case of the α -glyceride. This is of interest in showing the influence of the glyceryl radicle in the drying of vegetable oils.

The preparation of metallic tungates is of importance. A tungate drier is one in which tung oil is heated with lead and manganese oxides and, when the oxides are dissolved, previously-made resinsates of lead and manganese are incorporated. Such a drier is soluble in a drying oil (especially a fish oil) at temperatures above 100°C . For the preparation and properties of a number of metallic tungates reference may be made to Circular 120, P. and V. Manufacturers' Association, U.S.A. The addition of tung oil improves Portland cement paints, not only producing a flat surface, but one upon which a subsequent coat of paint will adhere better than on one without wood oil.¹⁸

Other Oils from Aleurites.—(i.) *Candlenut Oil*.—Candlenut oil from *Aleurites triloba*¹⁹ of Fiji, Hawaii, West Indies, and Brazil might be used to replace linseed oil in the manufacture of paint and linoleum, but it is more suitable for soap manufacture. Its low iodine value (137) indicates its inferiority for drying. S.g. is 0.927 at 15°C .; free fatty acids (oleic acid), 0.7 per cent; saponification value, 175. In Madagascar the oil expressed from the nuts is known as "bakoly" oil. In India it is called "lekuma" oil. It would find a ready sale if its transport to the consuming markets were feasible.

(ii.) *Lumbang Oils*.—Lumbang oil from *Aleurites moluccana* (lumbang bato nuts) and *Al. trisperma* (lumbang banucalag nuts), soft lumbang oil.²⁰ The first-named *Aleurites* is the commoner, the latter not being utilised, since it is said to cause skin eruptions on those handling the oil obtained therefrom.

Lumbang bato from the Philippines is stated to belong to the same species as the candlenuts from Fiji. Lumbang bato can be distinguished from lumbang banucalag by the insolubility of its oil in alcohol.²¹ The oils do not approach linseed oil in drying properties, particularly from *Al. trisperma*, but if the oils are mixed in the proportion of 1:1 or 1:3 lumbang bato and lumbang banucalag, very suitable results are said to have been obtained, using red lead as a drier. The drying and moisture-excluding properties are said to be nearly as good as those obtained by careful experiments with linseed oil. Soft lumbang oil resembles tung oil in odour and in body. When spread on glass it dries in thirty-four hours to an opaque crystalline film. It does not solidify at 280°C . in fifteen minutes although it becomes "bodied." Lumbang oils might be mixed with linseed oil when the price is satisfactory. The manufacture of lumbang oil is carried on in a most primitive manner by Chinese workers. In 1911 it was stated that a factory of the capacity of 230 metric tons per month could be kept supplied. The oil is used locally for caulking vessels, for soft soap, and in the manufacture of paints. There is a great demand for the oil in the

United States. The shell of the nuts, amounting to 66 per cent of the total weight, is very hard and tough and extremely difficult to remove, the operation being performed by hand, either after sun-drying and boiling with water or heating over a fire and quenching in water.²² A. P. West and Z. Monte²³ give the following description of the seeds of *Aleurites moluccana*: 66 per cent shell, 34 per cent kernel, containing 50 to 60 per cent of oil possessing s.g. 0.9206 (31° C.), I.V. 140 (Hanus). The oil is stated to consist of 6.5 per cent linolenic, 33.4 per cent linolic, 56.9 per cent oleic, and 2.8 per cent solid acid glycerides. It dries quickly, is not polymerised at 200° C.; and is free from elæostearic acid.*

Perilla Oil.—Perilla oil is expressed from the seeds of *Perilla ocymoides* (*Nankinensis*), Asiatic mint, an annual plant growing in China, Japan, and the East Indies. The seeds contain 38 per cent of oil, and both oil and cake are edible like linseed. In Japan it is employed as an adulterant of lacquer. Very little up to the present has been exported to the United Kingdom. The cultivation of seed is being studied in India, the East African Protectorate, S. Africa, Cyprus, and Rhodesia,²⁴ also in America and in Canada. A comparison with linseed oil is shown by Lanks²⁵ and by the writer:

	S.G.	Acidity.	I.V.	S.V.	Refractive Index.
Perilla oil	0.9343 (15° C.)	6.7	182.9 (Wijs) 196.206 (Hanus)	188.6 190.6	1.4841 (20° C.) 1.4840 (25° C.)
Linseed oil	0.932-0.9360 0.933-0.9340	..	180 174-184	..	1.4790 1.4775

* Perilla oil showed no "foots" on the breaking test, and the colour of the clarified oil was fair, whilst, linseed oil showed 3.3 per cent foots.

To test the drying properties of perilla oil compared with linseed oil, three paints were made containing white lead, zinc oxide and lithopone respectively, without addition of driers, and spread on a wood surface. In the case of the perilla oil paints, the drying time was seventeen hours, whilst of the linseed oil paints none dried before twenty hours. When driers were added, all the paints dried in about twelve hours and the perilla oil paints showed a somewhat harder surface. As a varnish with lead and manganese driers, perilla oil dried in a shorter time with a slightly better gloss than a corresponding linseed oil varnish. In other respects perilla oil compares very favourably with linseed oil.† In Circular 52 (P. and V. M. Assoc. of U.S.A.), the possibility of growing perilla for oil is considered. The perilla plant grows best in a warm humid atmosphere and, if planted in the early spring, may seed before the summer is well over. (It has been

* C. D. Holley (*Paint Vehicles, Japans and Varnishes*) states that cold pressed lumbang oil has s.g. 0.927 and refractive index 1.4750.

† K. H. Bauer concludes that perilla oil contains glycerides of palmitic, linolic, and probably several isomeric linolenic acids.^{26a}

grown already sufficiently well in a few States of North America to make it worth while continuing the cultivation. The plant is practically a weed in Japan. The writer considers that the water-absorbing power of the perilla oil linoleum film is very much less than that of linseed oil, and a smaller quantity of drier is required to cause the film to harden. The statement that it forms drops when spread on a surface is not generally accepted by users of the oil. If the perilla oil is too heavily charged with driers it will dry to a crocodile-like skin, which, however, does not form when the concentration of the driers is reduced. The rate of polymerisation is much less than that of tung oil and greater than that of linseed oil. It can be used with advantage as a diluent of tung oil.

It has none of the defects of tung oil in too rapid gelatinisation, nor do films containing the oil "web" like the corresponding tung oil films. It can easily be bleached by fullers' earth on heating up to 270° C. and does not darken afterwards.²⁶ The high acidity of the commercial samples causes retardation in the thickening on being heated. H. A. Gardner²⁷ reports favourably on the use of perilla oil in paints and in linoleum. The writer considers from his experience that it is a valuable substitute for linseed, possessing superior properties in many ways, but its high price compared with that of linseed oil will restrict its general use except for special varnish mixings. It is claimed that, when raw or improperly treated, it dries with a dull finish. This can be overcome by heating to 293°-315° C. for one hour or more if a heavier body is required. This treatment, it is said, gives an oil which will dry with a high lustre and without runs, makes a tough film, and will not spot under extreme weather conditions.²⁸

Soya Bean Oil.—The Soya bean (*Glycine hispida*) is indigenous to China, Manchuria, and Japan, where it grows prolifically. It was practically unknown in this country before the Russo-Japanese War. Since that time the use of oil and cake has spread phenomenally, but of late the demand has dropped, although the oil-cake is a rival of linseed and cotton cake as a cattle food. The oil belongs to the less active drying oils, although with suitable driers it has given very fair results.²⁸

H. Low²⁹ gives an analysis of Soya bean oil as follows :

S.G., 0.929; S.V., 190.201; Acid V., 0.8-3.1; Unsaponifiable Matter, 1.16; I.V., 124.30, 133.8.

Total fatty acids, 94.66 per cent. Combining weight of fatty acids, 279.30.

W. B. Smith³⁰ concludes that Soya bean oil contains 2.3 per cent linolenic acid, 55.57 per cent linolic acid, 26.27 per cent oleic acid, and 9.10 per cent saturated acids. The low iodine value, 130, with an ether-insoluble bromide value of 7.8, indicates that its oxygen-absorption power will be low.

Soya bean oil is in demand largely for edible purposes, but its use in paints and varnishes is limited. Its presence adds flow to a mixing, and it may be added to more strongly drying oils with advantage.

DIFFERS FOR PERILLA, SOYA, AND MENHADEN OILS COMPARED WITH
LINSEED OIL³¹

Metal Content of Oil, 0.1 per cent	Sediment.	Skimming Time.	Temperature of Incorporation.	Film.
Perilla Oil—				
Solid Co. Linoleate . . .	none	5 hours	450° F.	hard
Co. Mn. Linoleate . . .	slight	5 "	"	"
Cobalt Paste Drier . . .	"	8 "	cold	hard
Co. Mn. Paste Drier . . .	"	14 "	"	soft
Ppd. Co. Resinate . . .	none	6 "	450° F.	hard
Ppd. Mn. Resinate . . .	slight	14 "	"	"
Lead Linoleate . . .	none	20 "	"	"
Raw Soya Bean Oil—				
Solid Co. Linoleate . . .	none	24 hours	450° F.	medium
Co. Mn. Linoleate . . .	considerable	24 "	"	"
Co. Paste Drier . . .	none	8 "	cold	soft
Co. Mn. Paste Drier . . .	slight	8 "	450° F.	hard
Ppd. Co. Resinate . . .	"	11 "	"	soft
Ppd. Mn. Resinate . . .	"	40 "	"	medium
Lead Linoleate . . .	none	42 "	"	"
Light Pressed Menhaden Oil—				
Solid Co. Linoleate . . .	none	11 hours	450° F.	medium
Co. Mn. Linoleate . . .	slight	13 "	"	"
Co. Paste Drier . . .	none	13 "	cold	"
Co. Mn. Paste Drier . . .	considerable	13 "	"	"
Ppd. Co. Resinate . . .	slight	30 "	450° F.	"
Ppd. Mn. Resinate . . .	"	13 "	"	"
Lead Linoleate . . .	none	16 "	"	"
Raw Linseed Oil—				
Solid Cobalt Linoleate . . .	none	16 hours	450° F.	hard
C. Mn. Linoleate . . .	considerable	17 "	"	"
Cobalt Paste Drier . . .	"	5 "	cold	"
Co. Mn. Paste Drier . . .	slight	8 "	"	"
Ppd. Co. Resinate . . .	none	10 "	450° F.	"
Ppd. Mn. Resinate . . .	slight	15 "	"	"
Lead Linoleate . . .	"	22 "	"	"

It is possible to incorporate 25 per cent Soya oil with linseed oil, using a manganese, cobalt, lead drier, to give a mixing containing 0.03 per cent Mn., 0.01 per cent Co., and 0.20 per cent Pb. The films dry as rapidly as commercial boiled linseed oil containing 0.21 per cent Pb and 0.041 per cent Mn. It is advisable to blow the Soya oil first and to subject it to a heat treatment previous to the addition of driers. The Soya bean contains 18 per cent of oil from which 10-13 per cent can be extracted by the Anglo-American process. Against this low yield must be set the fact that the harvest of the bean is large and the press cake is rich in nitrogenous matter or proteins (39-42 per cent). Besides cattle cake it is made into biscuits, vegetable cheese, and a kind of pickle (soy). The emulsification of the oil with gluten and casein-like bodies is the basis of some patents for artificial milk.³² The emulsifying power seems superior to that of other drying oils. /

Para Rubber Seed Oil.—This oil, obtained from varieties of Para rubber seed kernels, has been thoroughly investigated at the Imperial Institute.³³

The Hevea rubber tree (*Hevea Braziliensis*) will produce on an average five hundred seeds per annum (one hundred seeds weigh 360 grams).

Ceara rubber seeds weigh about 53·2 grams per hundred, whereas the seeds of *Funtumia elastica* are small with thin soft husks.

Dubosc³⁴ states that the seeds of Hevea contain 52 per cent of oil and yield 33 per cent in a single pressing, but this must refer to decorticated seeds, because R. J. Eaton³⁵ obtained 19·3 per cent from the whole seed by extraction with a volatile solvent. The following table gives a comparison of the three varieties of Para rubber seed oil and linseed oil :

	Ceara.	Funtumia.	Hevea Braziliensis.	Linseed.
Wt. of 100 seeds . . .	53·2	4·8	360 grams	..
Percentage oil - content of kernel . . .	35	..	45·8	..
Percentage oil - content of whole seed . . .	15·75	31·0·33	22·25, 19·3	36·4
Sp. gr.	0·9238	0·9320	0·9258	0·931·8
"	1·475	1·4788	..	1·4835
Relative viscosity . . .	13·0	14·3	..	18·0
I.V.	135·137	138	131·138 138·7	180·200
Acid value	0·625	2·65	5·26, 16·8	below 5
Percentage of liquid fatty acids	88·9	79·8	86	92·5
I.V. of liquid fatty acids	162·5	175·5	..	190·200

The oil from Hevea is of yellow colour and deposits little or no stearine. The oil is not equal to linseed oil for paints and varnishes ; its lead drying oil is slow drying, giving a soft film. Using a cobalt drier the drying is also unsatisfactory and the film is tacky even after several days.³⁶ If the oil be heated with glycerine and calcium resinate at 260° C. for 1½ hours the acidity is reduced to 5·1, and the neutral mixing with a cobalt drier (sufficient to reduce the drying time of linseed oil to six hours) gives a film which resembles that of Soya, but is decidedly inferior to that of linseed oil.)

The water-absorbing power of the lead drying oil film is much greater than that of linseed oil. A drying oil containing 3 per cent lead oxide made from linseed and Para rubber seed oils respectively dries in five hours and seven hours, and the latter film holds a tack even after four days.

(It is evident that the oil has none of the protective properties that the latex will give. It would be suitable for soap making, and could replace linseed oil in the manufacture of rubber substitutes.)

Probably it would be suitable for the preparation of hydrogenated or hardened oils for edible purposes. The cake left after extraction of the oil from the kernels is a valuable foodstuff for sheep or cattle.

R. J. Eaton (*loc. cit.*) obtained 19.3 per cent of oil, 76.6 per cent of meal, and 2.93 per cent of mucilage foots. He concluded that it would be remunerative to import into this country for crushing. His estimate of the cost of shipping (£1:15:10 per ton) could be reduced by half if the seeds were decorticated before being shipped. The *Imp. Inst. Bulletin* gives the cost of decortication as 12s. 6d. per ton and cost of collection as £2:18:4 per ton, with rail and freight charges of £3:15s. per ton. Therefore the seed would probably cost from £9 to £10 per ton in this country. In 1917 the oil fetched £50 per ton, when linseed oil was £60. It would seem advisable to be guided by Eaton's estimates, which are later. The quantity available is satisfactory, and Eaton estimates that 26,000 tons of oil could be obtained annually from seed grown on the Malay Peninsula.

To the varnish maker Para rubber seed oil stands in much the same position as Soya oil, and with present knowledge it does not seem to have any prospect of displacing linseed oil in general drying and protective properties.

Other oils which are used in small quantities in paints and varnishes are: Walnut, Poppy, Niger, Sunflower, Hempseed, and two new drying oils, Chia and Oiticaca oils.

Walnut Oil.—This is a very pale oil used by artists, because paints made with it have less tendency to crack than those containing linseed oil.

Poppy Seed Oil.—The seeds of the opium poppy (*Papaver somniferum*) contain 40-50 per cent of an oil containing 65 per cent linolic acid, 5 per cent linolenic, and 30 per cent oleic acid. It is a pale oil and fair drying, but used more in artists' colours than in paints and varnishes.

Niger Oil, Sunflower Oil, and Hempseed Oil possess drying properties whereby they may be used in paints and varnishes, but they are inferior to linseed oil. Seven years ago India exported over 10,000 tons of niger seed in a year, but the export trade during the war dwindled to almost nothing, though the seed is still grown and the oil is used in India in large quantities for cooking and lighting and as an adulterant. Provided the price of linseed oil is not much above that of these oils, the demand for them by the paint and varnish maker is very limited. They are mostly used for soap-making or edible purposes. For details as to their properties reference may be made to Fryer and Weston (*loc. cit.*).

Chia Oil.—The seeds of, *Salvia hispanica*, a labiate, are widely cultivated and grow wild in Mexico, where they are known as chia or chian; they are used for making a demulcent drink, somewhat like "flaxseed tea." Travellers carry the seed to mix with water, as it has been observed that the thirst is quenched with much less water when chia seed has been mixed with it. The chia plant

is a plant which reaches 5 to 6 ft. high; the seeds are oval-shaped, about 1 mm. in longest and about $\frac{1}{2}$ mm. in shortest diameter. The yield per hectare varies from 1000 kilos to 4000 kilos, and in certain parts of the country two crops may be obtained annually. The seeds yield a yellow oil in amount equal to 33 per cent of the seed expressed. The examination of the filtered oil gave: s.g. (15° C.), 0.9338; acid number, 0.6; iodine value, 196.3; S.V., 192.2; unsap. matter, 0.8; n_D , 1.4855.

In the raw state the oil dries slowly. It exhibits more pronounced "crawling" than raw perilla oil, indicating that chia oil has a high surface tension. This defect disappears on heating the oil to 260° C., and in this condition it was found to be superior to linseed oil when treated with the same amount of drier.

From the comparison of wetting power with pigments it would seem as if chia oil would yield more heavily-bodied paints than linseed oil. The success of the oil will depend on the value of the press cake compared with linseed cake.³⁷

Oiticica Oil.—Bolton and Revis³⁸ have described the oil extracted from the kernels of *Oiticica* (*Conepia grandifolia*), indigenous in Brazil. The kernels are one inch long and half an inch broad, and are stated to contain 62 per cent of oil, semi-solid at the ordinary temperature (m.p. 21.5° C. incipient fusion, 65° C. complete fusion), consisting of a solid fat in a medium of liquid oil. In many respects it resembles tung oil, yielding no solid hexabromide, and possesses a high specific gravity (0.9694) and an iodine value 179.5. It does not solidify when heated for thirty minutes at 250°-270° C. in carbon dioxide, but when the temperature is raised to 300° C. gelatinisation occurs. At 100° C. it gains 4 per cent in weight in air in three hours, and in twenty-four hours the total gain in weight was 4.5 per cent, whereas tung oil gained 2.3 per cent under the same conditions. The skin produced is more uniform, transparent, and continuous than from tung oil. The refractive index (40° C.) is beyond the limit of the Zeiss butyro-refractometer. The melting point of the fatty acids is 53°-7.67° C. The writer has found that cold benzol extracted only 29 per cent of oil from the sliced kernels. The specific gravity of the oil varied from 0.94-0.9786 and the iodine value from 150-170. The oxygen absorption in thirty-nine days gave an increase in weight of 7.38 per cent, whilst tung oil showed an increase in weight of 14 per cent in thirty-two days. The oil could be heated at 270°-280° C. without gelatinisation. An analysis of the kernels after removal of the oil by benzol gave the following figures:

Moisture, 7.08; oil, 17.35; albuminoids, 11.07; carbohydrates, 56.07; fibre, 4.81; ash, 3.62=100.00.

The potassium salt obtained from the oil is very soluble in water and gives a crystalline acid, m.p. 98°-99° C., which is not an elaeostearic acid. The properties of the oil appear to be promising, as it is free from the difficulty of rapid gelation on heating, but it is oxidised so rapidly in the air that a crushing process is inapplicable

and extraction methods on the large scale have not as yet been successful.

Fish Oils.—Although whale, shark, dog-fish, and herring oils have been used to some extent in the manufacture of paints, menhaden oil has proved much more satisfactory. The production from *Alosa menhaden*, a fish resembling a herring (*Alosa menhaden* is obtained off the Atlantic coast line of N. America from N. of Chesapeake Bay to Florida), amounted to 3,943,000 gallons in 1918. The quantity depends on the activity of the fisheries. It is cheaper than the vegetable drying oils and has been used in the adulteration of paints or for leather-cloth or oil tablecloths in the U.S.A. In the paint and varnish industry it is not popular in this country, because of its odour and general inferiority to linseed oil. The raw fish oil never dries permanently hard and has a tendency to become soft in a warm, moist atmosphere. For general outside work, especially on the sea coast, and for application on hot surfaces, it is suggested that a mixture of menhaden oil with linseed up to 75 per cent of the former might be employed. Toch³⁹ recommends its use in paints for structural steel and other metals. An advantage claimed for the oil in combination with linseed oil is that the mixture is more impermeable than linseed oil alone to the action of water. Another advantage claimed is that it has the power when dry to give a film of great heat-resisting power, and hence it has been recommended for use in smoke-stack and boiler paints. Jensen⁴⁰ states that the fishy odour can be removed by catalytic treatment, whereby the oils are now in increasing demand. The smell is undesirable, and is said to be due to the presence of clupanodonic acid and trimethylamine.

It is very difficult to remove the smell except by hydrogenation, which lowers the iodine value and the drying properties, besides increasing the viscosity. Heat treatment, especially in the presence of driers, reduces the odour. Methods for deodorising fish oils include the use of ozone, sulphuric acid, heating *in vacuo*, treatment with alcohol, sodium hypochlorite, alkalies, etc. All these processes are expensive and not very practical. Gardner⁴¹ recommends the addition of 5 to 10 per cent pine oil as a deodoriser. The oil may be refined by fullers' earth, china clay, copper hydroxide, and charcoal. Weiss⁴² claims that the oils may be deodorised by treatment with a fine jet of steam in the presence of alkali. It is stated that paints made with suitable proportions of menhaden, soya and linseed oil with varnish resins and the usual driers, have yielded coatings which are equal to and even superior to those produced with linseed oil alone.⁴³ It is quite evident that menhaden oil may be used as a limited substitute for linseed oil. The use of fish oils, other than menhaden and sardine oils, in paint manufacture is unsatisfactory, and as they are in large demand for other purposes, unless there is a shortage of linseed oil, there would seem to be nothing gained by employing them. They are more or less dark in colour and cannot be regarded as drying oils, but blown herring oil has proved a serviceable constituent of heat-resisting paints

and those required for counteracting the corrosive effects of sea air. Toch states that linseed and fish oils are able to digest a larger proportion of red lead than linseed oil alone.

The Composition of Menhaden Oil.—E. Twitchell⁴⁴ states that the fatty acids obtained from menhaden oil contain 22.7 per cent palmitic acid, myristic acid 9.2 per cent, stearic acid 1.8 per cent; total saturated acids, 33 per cent: unsaturated acids, containing 18 carbon atoms, 24.9 per cent; containing 20 carbon atoms, 22.2 per cent; containing 22 carbon atoms, 20.2 per cent. The presence of such a considerable amount of saturated acids will go far to account for the tackiness of the dried films of the oil.

M. Tsujimoto⁴⁵ considers that elupanodonic acid should have the formula $C_{22}H_{34}O_2$, as it yields a decabromide $(C_{22}H_{34}O_2Br_{10})$, and not $C_{18}H_{26}O_2$ as previously given by him. He states that the lithium salts of highly unsaturated fatty acids are soluble in acetone containing a little water (5 per cent by vol.), whereas saturated and less saturated acids give insoluble lithium salts. Vegetable oils and terrestrial animal oils give only relatively small yields of highly unsaturated fatty acids; e.g. 1.2 per cent in sesame oil and 9.3 per cent in linseed oil.

Linseed Oil Fatty Acids.—During the Great War the demand for glycerine together with the general shortage of fatty oils resulted in the acids from linseed oil being tried as a substitute for the glycerides in paint and varnish manufacture. As a preliminary step it was advisable to separate the more saturated acids, e.g. stearic acid, which were in suspension. The fluid portion could be thickened with only slight loss by special methods to yield lithographic oils of low grade, which in emergency might find application in printing inks. For drying liquors and binding sizes favourable results were obtained. When used with pigments of an inert character inferior quality paints were obtained, and although gloss and general appearance were fairly satisfactory, the durability was poor compared with linseed oil paints. When iron turnings and fatty acids were brought in contact in the presence of water, a red brown liquid containing 3.4 per cent iron (75 per cent in the ferric condition) was obtained. This liquid had the property of drying in air like a boiled oil and as such could be used with oxide of iron, umbers, ochres, blacks, and other inert pigments to give fairly durable paints. Medium stoving and stamping varnishes, as well as japans and black enamels, could be prepared, but their resistance to weathering and to the action of water was poor and they lacked elasticity and body. The experience of their use in the dressing of waterproof sheets and tarpaulins was unsatisfactory. Cotton sheets were found to be better than flax sheets, probably owing to the greater absorbing power of the former, but they were decidedly less impervious to water, drying hard and stiff and developing a tackiness when the sheets were folded.⁴⁶

Bevan⁴⁷ removes stearic acid by a limited treatment with lime and then adds cobalt resinate as a drier. Wilkins and Allsebrook⁴⁸ describe the action of metals, e.g. iron, on the linseed oil acids.

Boehm and Reihl⁴⁰ claim to heat the linseed oil acids to a high temperature in the presence of metallic copper, nickel or cobalt, and to blow in oxygen until a sp. gr. of 0.992-0.998 is obtained. It is an advantage to add 12-15 per cent of tung oil and a small quantity of an alkaline earth soap to increase the speed of polymerisation.

The comparison of the true oxygen absorption curves of linseed oil and its fatty acids gave 28.7 per cent and 30.1 per cent respectively, although in the latter case the period of induction was much shorter. The form of the curves is the same, showing that the glyceryl radicle has no influence on the *modus operandi* of the oxidation (see Figs. 11A, 11B, and 11C, pp. 30, 31, 32).⁵⁰

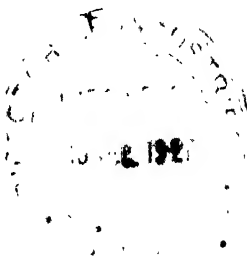
Copals are easily soluble (even when unsweated) in the linseed oil fatty acids, but the solution on treatment with turpentine gives a precipitate of the copal resin. It is only after the gum has been run in the oil-acids in the ordinary manner that the mixing will stand thinning with turpentine or petroleum spirit. Linseed oil acids may be used as a solvent for rubber.

Drying Oils from Petroleum and other Hydrocarbons.—By chlorinating the hydrocarbons of the so-called neutral oils and removal of the chlorine introduced, Gardner and Biellouss⁵¹ state that oils are produced equal in drying power to linseed oil, but their colour is dark and the durability inferior to that of linseed oil. When heated to high temperatures they are polymerised to solid elastic bodies. Much careful investigation will be required before these substances can displace linseed oil.

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CHAPTER VI

VARNISH RESINS

THE majority of the resins used by the varnish maker are of vegetable origin, being exudations of trees of many different genera and species. It is only recently that artificial resins derived from coal tar products, *e.g.* Bakelite, Cumarone, and Para-indene resins, have been used as substitutes. For oil varnishes the natural resins are preferred. The varnish resins belong to the class of gums which are for the most part exudations of living trees or come from the secreted resins of fossil trees. These gums, sometimes alone, but often incorporated with a fluid, form more or less protective films on the escape of the solvent. They show generally the properties of colloids when in solution, except in alcohol, and form emulsoid solutions with water, oil, and other media. Some are completely soluble in water, others swell up to give jellies, whilst others are unacted on. It is with members of the last class that the varnish maker has to deal. The colloid properties of the gums are in many respects similar to those of glue and gelatine. The resins can be readily distinguished from the true "gums" by the following simple tests: (1) When a resin is held in a flame it takes fire and burns with a smoky flame giving off an aromatic odour. A gum similarly treated chars and smells of burnt sugar; (2) a resin placed in water is unaltered, whereas a gum dissolves or forms a jelly; (3) when a resin is allowed to stand in methylated spirit or in turpentine, it disintegrates or dissolves completely or partially. A gum is generally unacted on by these solvents.¹ L. Paul² considers that the resin substances occupy an intermediate position between inorganic colloids and bio-colloids. The colloid modifications of the true constituents of resins are analogous to inorganic dispersions, which are colloidal modifications of crystalloid substances.

Although only the resins are the important gum ingredients of varnishes, a passing reference to the true gums, by way of contrast, is advisable. The varnish terms, gums, gum resins, etc., are restricted to the resins and have nothing to do with gum arabic, cherry gum or gum tragacanth. Gum arabic and gum tragacanth can be taken as typical for purposes of comparison.

Gum Arabic.—Gum arabic is obtained from varieties of *Acacia* and is known in the trade under many forms, *e.g.* Turkey, White,

Kurachee, Mogador, Wattle, and Senegal. These forms are all more or less soluble in water and swell up in that medium. They are insoluble in alcohol, and on boiling with dilute sulphuric acid give sugars (pentoses and hexoses), thus showing their carbohydrate nature. The best qualities are used for pharmaceutical preparations, confectionery, and other purposes, whilst the commoner qualities are in demand in the textile industries, as a binding material for artists' water-colours and for mucilages.

Gum Tragacanth.—Gum tragacanth is obtained from various species of *Astragalus*, indigenous to Greece, Asia Minor, Syria, and Persia. The gum flows freely from the stems where they are wounded. It is softer than acacia and cherry gums. Like gum arabic it gives a viscous fluid with water and is hydrolysed with dilute sulphuric acid to give sugars. It is used as a thickener in calico printing and as a vehicle in many pharmaceutical preparations.

BALSAMS AND OLEORESINS

The balsams are solutions or emulsions of resins in oil esters, e.g. the esters of cinnamic or benzoic acids, and they may contain also free cinnamic and benzoic acids. The oleoresins consist of resins dissolved in essential oils. It is, however, difficult to draw a hard and fast line between the two classes by differences in the nature of the resin solvents. The balsams are essentially more fluid than the oleoresins, although certain varieties of oleoresins when freshly exuded have considerable fluidity, so that the oleoresin may be said to be exuded in the balsamic form, hardening on exposure to the viscous solid oleoresin. Canada balsam is classed amongst the oleoresins rather than the balsams. The transformation of a balsam into an oleoresin may be a combined oxidation and polymerisation process. It may resemble the transformation of the latex into the solid rubber. The differences are perhaps rather of degree, although balsams often contain a high percentage of oil esters. Reference may be made to several of the commoner balsams for purposes of comparison, but the varnish maker does not handle these substances.

Copaiba Balsam.—This contains as much as 60 per cent of oil esters and is the exudation of different varieties of *Copaiferae* occurring in S. America, Brazil (San Paulo), and Guiana. The production is simple. The tree stems are cut into as far as the reddish-brown heart, and in a short time the balsam flows in quantity (up to 50 litres) and is collected. The balsam may be fluid (s.g. 0.935-0.936), or a viscid fluid as Maracaibo balsam. It is composed of an ethereal oil, 40 to 60 per cent, which may be distilled off and a resin, 40-60 per cent, which contains crystalline acids, and in different resins. Commercial paracopaiba balsam (s.g. 0.92-0.95) is a thin liquid, colourless, darkening on keeping, with a bitter taste and peculiar balsam-like odour. The Brazilian varieties have an almost turpentine-like smell. They are soluble in alcohol, ether,

and benzol. The adulterations comprise turpentine, rosin, and castor oil. The balsam finds little use in varnish manufacture.

Gurjun Balsam.—Gurjun balsam is obtained from varieties of *Dipterocarpus* in Burma, Java, and Ceylon. In Burma the collection is simple: two or three holes are made at the base of the tree and the trunk is warmed. The holes are emptied every three or four days, and the holes remade. From two or three holes in the tree 30-40 gallons of oil are obtained in one year.³ Gurjun balsam consists of a resin and an essential oil (40 to 82 per cent) which is a sesquiterpene ($C_{15}H_{24}$, b.p. 225° - 256° C.). Comparison may be made with the composition of the pine oleoresin (p. 101) and also with the copal oils obtained from the distillation or sweating of copal resins, whereby depolymerisation ensues. A similar comparison may be made with Venice turps, which has been obtained artificially from rosin, rosin oil, and turpentine. The more fluid balsams pass by polymerisation rather than oxidation to the viscous and eventually solid oleoresins, especially as a balsam hardens by treatment with magnesia and alkaline earths, as is the case with colophonium and the copal oils. Towards solvents Gurjun balsam behaves like the Copaiba balsam. In Java and Ceylon it can be used as resin lacquer much like Canada balsam.

Other important balsams are Peru (San Salvador), Mecca, and Tolu balsams. Storax (liquid form, derived from *Liquidamber styracifica*) from Mexico and Honduras,⁴ contains styrolene, cinnamic acid, cinnamyl cinnamate, styracine, pyrocarpene and a resene. E. Fourneau and M. Crespo⁵ suggest alcoholysis in the study of balsams, e.g. by boiling with alcohol containing hydrochloric acid, whereby the resins are unattacked whilst the free acids are esterified. In the analysis of Tolu balsam from S. America, T. Cocking and J. D. Kettle⁶ recommend boiling with water and magnesia with the addition of a small quantity of xylol to soften the resinous matter; the magnesium salts of the aromatic acids are soluble in water, whilst those of the resin acids are insoluble. Trommsdorf found: resin 88 per cent, acids 12 per cent, and volatile oil 0.2 per cent. The balsams described find their use in pharmacy.

OLEORESINS

It is difficult to separate the resins from oleoresins for purposes of classification. Ordinary rosin is obtained from the fluid oleoresin tapped from trees of the genus *Pinus*, the volatile spirit being oil of turpentine. The fluid oleoresin has many names, e.g. turpentine, *terébenthine*, terpentine, gum thus. Similarly the volatile oil is oil of turpentine, *essence de terébenthine*, *terpentinöl*, and turps. Venice turpentine, Strasbourg turpentine, Canada balsam, Bordeaux turpentine, galipot, are names given to local varieties of the oleoresin (galipot is a hardened oleoresin from the Landes district of S.W. France). Elemi, Dammar, Mastic, Sandarach are various forms of oleoresins, which flow by wound response of the stem and gradually harden on exposure to air.

Pinus Oleoresin.—The most important oleoresins are those derived from varieties of *Pinus*, and owing to the increasing use of China wood oil they are becoming more and more popular for varnish making. When incorporated with linseed oil the resin, after removal of the volatile oil, gives a coating of inferior durability, but by substitution of tung oil for linseed oil an excellent protective coating may be obtained.

Bordeaux Turpentine.—This oleoresin is obtained from *Pinus maritima*, which is cultivated on the sand dunes of the Landes district (Gironde and Gascony). The cultivation has been greatly developed since the end of the 18th century. The growth of the tree is so rapid that it attains a diameter of nearly a foot in twenty-five years, and the secretion is so abundant that in some cases collection is begun when the trees are barely fifteen years old, as in the case of the so-called clearance trees, which have to make room for those reserved for longer tapping. The collection of the resin is begun normally at the 20-30th year and may continue to the 75th year. The area under cultivation in 1909 was 750,000 hectares. The development of the industry has progressed more in France than in the United States. The French method of collection is much more economical and less destructive to the tree, which has therefore a longer lease of life and consequently is far more productive. A comprehensive account of the French turpentine industry is given in a paper by A. Joly,⁷ of which the following is an abstract.

Morphology of *Pinus maritima*

The Flowers.—The *Pinus maritima* has male and female flowers on the same stem. The male flowers consist of an enlargement composed of small pockets full of pollen, which spread themselves over the female flowers in the shape of small herbaceous cones covered with fine drops of resin to which the pollen adheres. The pollen grain consists of a body furnished with two small air sacs, and on adhesion it puts out a germinative tube, but does not fertilise the ovule until the following year. The fruits, *pommes de pin*, consist of cones which attain to a length of 8-15 cm., with a rough lozenge pattern surface. Each angle of a lozenge is connected with a hard woody shell which protects the seed. These fruits become ripe towards the end of the second year, and the seeds become detached in April. The gathering of the seeds takes place usually in March, in the case of carefully selected full-grown trees. The *pommes de pin* are submitted to a gentle heat (50°-55° C.) in order to distend the shells and to allow the seed to detach itself easily.

The Seed.—The seed is provided with a membranous extension which has to be crushed. The actual seed consists of oily albuminous material, longitudinally crossed by an embryo which has usually seven cotyledons and is covered by two membranes, a thin endocarp, and a hard woody epicarp. From this seed it is possible to extract

15 per cent by weight of a drying oil (s.g. 0.928).^{* 8} It has been pointed out that *Hevea Braziliensis* seed yields a drying oil (Para rubber-seed oil). The germination does not take place until a month has elapsed, and then the young pine shows a small pivoting root and seven seminal leaves of triangular section.

The Leaves.—*Pinus maritima* has four varieties of leaves; (1) the seminal leaves of triangular section with a single libero-ligneous fascia; (2) the first year's leaves, which are isolated, thin, short and filiform; (3) the bracteate leaves; (4) the ordinary leaves, needle-shaped, with a striped semicircular section, their length varying from 10-20 cm. and their thickness 1.1-5 mm. If one examines a transverse section under the microscope one finds on its edge a sclerous envelope which gives rigidity to the needle. This envelope is perforated by stomata, which penetrate as far as the chlorophyllic tissue, whose cells are folded over in a characteristic manner. Towards the centre is found an endoderm consisting of cells flattened and corrugated in their lateral walls. In the centre of this endoderm one finds two liberoligneous fasciae with the wood turned towards the plane surface. Finally, the chlorophyllic parenchyma contains a variable number of resin ducts (two to nineteen) surrounding the endoderm. In certain cases these needles are submitted to distillation, but after some experience the idea has been conceived of making a vegetable horsehair from them, washable and undecomposable. It has been considered advisable to mention the seeds and leaves in detail because of later reference to their resinous content in connection with other varieties of *Pinus* (Douglas fir).

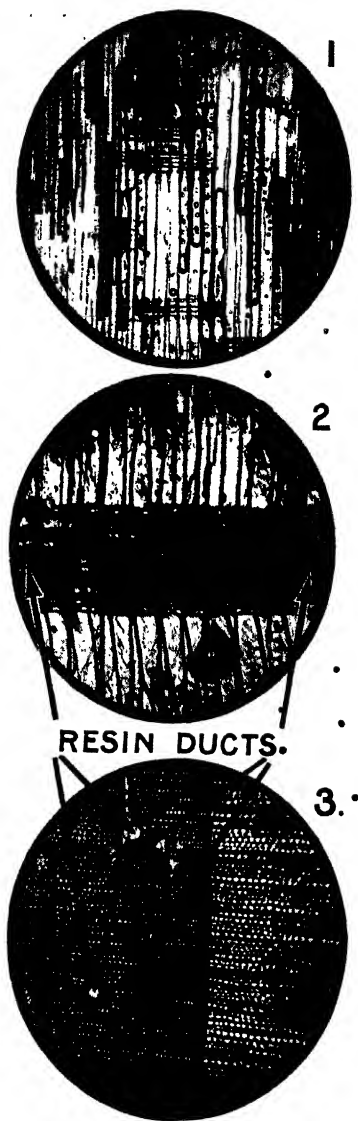
The Wood.—Under the microscope three tissues only are seen; the tracheids, the medullary rays, and the resin ducts.

(1) *The Tracheids* (Fig. 21 (1)).—In a longitudinal radial section the tracheids are found in the shape of ligneous shells, very elongated, entirely prismatic and enclosed, and terminated by a bevel at both ends. In the spring wood their walls are thinner and more separated than in the summer wood, where they appear thickened and with only a small space between them. The walls of the tracheids are marked with a series of small discs lenticular in shape, which have an opening in their centre. These discs are joined together and separated from each other by a permeable membrane, which permits the sap to circulate from one cell to another. Finally, the tracheids are crossed perpendicularly by the medullary rays.

(2) *The Medullary Rays* (Fig. 21 (2)).—The medullary rays consist of a group of rectangular cells superposed so as to form one single column and radiating from the circumference towards the centre in varying lengths. The cells are perpendicular to the tracheids, and those which form a connection with the tracheids are bevelled.

^{*} The oil from seeds of *Pinus sylvestris* contains 3 per cent solid acids (palmitic and stearic) and 97 per cent fluid acids (36 per cent oleic acid, 56.2 linolic acid, and 7.6 per cent linolenic acid) having I.V. 159.2 and S.V. 190.7.

(3) *The Resin Ducts* (Fig. 21 (3)).—The transverse section shows the difference between the tracheids of spring wood and those of summer wood, this latter being dotted with resin ducts. The medullary rays are represented by black lines. The ducts intended to convey the resin are found (a) in the wood of the root and of the stem; (b) in the cortical parenchyma of the branches; and (c) in the leaves. They are vertical and parallel with the axis of the trunk. A transverse section shows a duct surrounded with large parietal cells, where the resin is formed by means of a process which is still obscure. These parietal cells are surrounded by others of the same shape and more flattened, beyond which there is a ligneous parenchyma containing amylaceous cells and surrounded by the tracheids. Finally, the medullary rays themselves contain small resin ducts which are tangential and perpendicular to the large vertical ducts. They are full of resin, especially on the side leading from the large ducts towards the circumference. This accounts for the small depths of the grooves made during the operation of "gumming." If the sections mounted for microscopical examination be treated with acetate of copper, the resin ducts become stained yellow and are clearly discernible. The oleoresin is not like ordinary sap. The pine has a sap which is a water solution, quite different



• FIG. 21.—Sections of *Pinus maritima*.

chemically from oleoresin. The sap circulates between the roots and leaves through the fibrous cells of the sap wood and also through the cells of the soft inner bark. The oleoresin is associated with excess of materials not used up in the production of wood, leaves, and bark, but stored inside the wood.

The Gemmage.—The resin originating in the large cells of the resin ducts has a tendency to reach the circumference by means of the small resin ducts of the medullary rays tangential and perpendicular to them, so that a superficial incision made in the trunk of the tree allows the extraction of the maximum amount of resin. The parts nearer the circumference are richer in resin than the central part. The tapper (*gemmeur*) performing the operation of pricking (*piquage*) stimulates the section of the vertical resin ducts and lays bare the small ducts of the new medullary rays.

• *The Carres.*—The incision made on the trunk of the *Pinus maritima* is called a *carre*. The size of the incision is regulated by the *Administration des Forêts*, and should not exceed 8.9 cm. in length and 65 cm. in height per annum, which means about 3.50 metres (11.6 ft.) in the fifth year, when the work of a *carre* is ended. The depth should not exceed 1 cm. These measurements are carefully controlled by means of a three-dimensional calliper (*carrimètre*).

The distribution of the *carres* is arranged out with the greatest care. The first *carre* is performed on the thickest part of the tree, which is usually on the east side. It is carried out for three or four years until the annual incision reaches a height of 60 cm.

After giving the tree several years' rest, the second *carre* is made. This takes place at a point 120° N.W. of the first. The second *carre* and those which succeed it are carried out in the same manner as the first. The third is made at a point 120° from the second on the south side, the result being that these three *carres* form the corners of an equilateral triangle. The fourth, which is opposite to the third, is made at a point 60° N.E. of the first, the fifth at the point 120° of the fourth, and so on up to the eighth.

• There are several kinds of gemmage :

(1) Gemmage by exhaustion, applied to clearance pines. This is usually performed on trees fifteen years old, which are exhausted in four or five years, after which they are cut down so as to admit air around the pines which will require longer treatment.

(2) Perpetual gemmage (*à vie*), consisting in moderate incision in pines thirty years old, during a period of any length broken by long intervals of rest.

(3) Gemmage by exhaustion, preceding the razing to the ground, is performed on old trees marked for cutting down twelve years later.

(4) *Gemmage à mort*, in which case the tree will be exhausted in one or two years.

• The tapper's (*gemmeur*) tools comprise a *sarclé à peler* for removing the rough part covering the living bark at the point where the *carre* is to be made. The *habchott* is a kind of

hatchet provided with a handle $2\frac{1}{2}$ feet long with a curved blade. The *barrasquite* or *rasolet* is a tool shaped like a curved gouge, provided with a long handle much like the *sarcel à peler*. It is used for pricking (*piquage*) the upper part of the *carres*, i.e. for deepening the grooves cut. Formerly this operation was accomplished by means of the *habchott*, and the *gemmeur* used a ladder called a *crabe*, which was a pole provided with several steps and forced into the ground. Of the two processes used for the recovery of the gemme the one called *au pot* is the only one in use nowadays. In this process a transverse incision is made across the *carre* by means of *pushcramps*. This groove is intended to receive a sheet of zinc, furnished with cramps, beneath which is placed a pot of glazed clay for holding the gemme. Sometimes covered pots are used to avoid evaporation of volatile components of the gemme. The gemme which has dried and hardened on the cramp is called *galipot*. The gemme and galipot are collected and placed in large wooden bowls. One *carre* can yield 1500-2000 c.c. per season. The Bordeaux turpentine fresh from the tree has a disagreeable odour and an acid, bitter taste. It is a thick, transparent liquid, which subsequently becomes cloudy and viscous. On the average it contains—

Oil of turpentine	15-20 per cent.
Dry products	70-80 „
Water	10 „
Sand and impurities	2 „

The collection of resin is made five or seven times during the season, but the last collections are much less rich in turpentine oil than the first. In the French process the trees are worked when they are twenty-five years old and cuts continued until they have reached saw-mill size, i.e. when they are seventy-five years old. The trees are then felled by a travelling saw-mill and there is a second growth in the same area immediately afterwards. In the United States a given tract of country is worked only for six to ten years, but the exhaustion of the trees is much more rapid. It is to avoid this exhaustion of the pine forests that the French system of tapping has been recently investigated by the U.S. Government.

Tschirch and Weigel give the composition of the gemme as follows :

Resinic acids	64 per cent.
Essential oils	25-29 „
Resene	5-6 „
Various	1-2 „

Tschirch and Bruning, on treatment of Bordeaux resin with sodium carbonate, obtained a soluble part, 64 per cent, which on treatment with ammonium carbonate gave a mixture of soluble pimaric acid, $C_{14}H_{22}O_2$, 6 per cent, and two acids insoluble in ammonium carbonate, viz. pimaric acid, $C_{20}H_{30}O_2$, 8 per cent, and 48-50 per cent of α - and β -pimarolic acids, $C_{18}H_{26}O_2$. The part insoluble in sodium carbonate consisted of 25-26 per cent volatile

$C_{10}H_{16}$ and 3-4 per cent less volatile $C_{10}H_{16}$, with 5-6 per cent *bordéresène*. The distillation of the oleoresin comprises the turpentine and rosin industry, which will be referred to in detail later.

American Oleoresin, Turpentine, Gum Thus.—The most important American varieties of turpentine-yielding pines are *Pinus palustris* (Southern longleaf yellow pine), *Pinus taeda* (loblolly pine), and *Pinus caribaea* (Cuban or slash pine). Central America is as yet an undeveloped area (Mexico and British Honduras), but *Pinus ayacahuite* (Mexican white pine) flourishes there. It must be pointed out that the oleoresin is found in all varieties of pine, but only a few give a flow of sap after the incision of the bark; thus the Douglas fir (British Columbia) does not give any yield of oleoresin on tapping, but turpentine may be obtained by steam or by destructive distillation.

Morphology of *Pinus palustris*.—The morphology of *Pinus maritima* has been described especially in reference to the occurrence of the oleoresin in the wood. It is advisable to give a short account of the location of the gum in the American *Pinus palustris*. The oleoresin is located in so-called "resin passages" or spaces between the wood cells, as shown in Fig. 22. The cells which are to yield gum are formed from the cambium layer, the narrow ring of soft, delicate cells which lies between the bark and the wood, Fig. 22. During the growing season the cambium forms bark on the outside and on the inside the wood of the new annual ring by the division and growth of its simple cells into more specialised wood cells which develop variously into wood fibres (T), ray parenchyma cells (MR), and other parenchyma cells (GP), Fig. 22. The special thin-walled or parenchyma cells of pine, which are associated with gum production, occur in groups or clusters which frequently split apart at the centre to form more or less open spaces, the so-called resin ducts, canals, or passages. Although the heart wood is found to contain a higher percentage of resin, it is in the sap wood that the resin is produced. The actively gum-yielding clusters of parenchyma cells are found under the bark in the outer layer made up of a varying number of the annual rings of the wood. They remain alive longer than the other wood cells or fibres, and are able to grow and act upon the materials that are brought into them, or stored in them, during the growing seasons. The wood fibres or tracheids, although dead in less than a year after they originate at the cambium, function nevertheless in the sap wood, somewhat like water-pipes, in the conduction of the sap. The yield of gum depends very largely upon the health and activity of the thin-walled resin-producing parenchyma cells in the pine sap wood. If well treated the yield of oleoresin is high; if killed, the source of supply is lost. By stripping off a piece of bark and laying bare one square inch of the sap wood of long-leaved pine 300-400 horizontally extended rays would be exposed, each containing resin ducts or cells. The wounding of the tree appears to stimulate the activities of the living parenchyma cells already present. This response to wound stimulus is noticeable in early

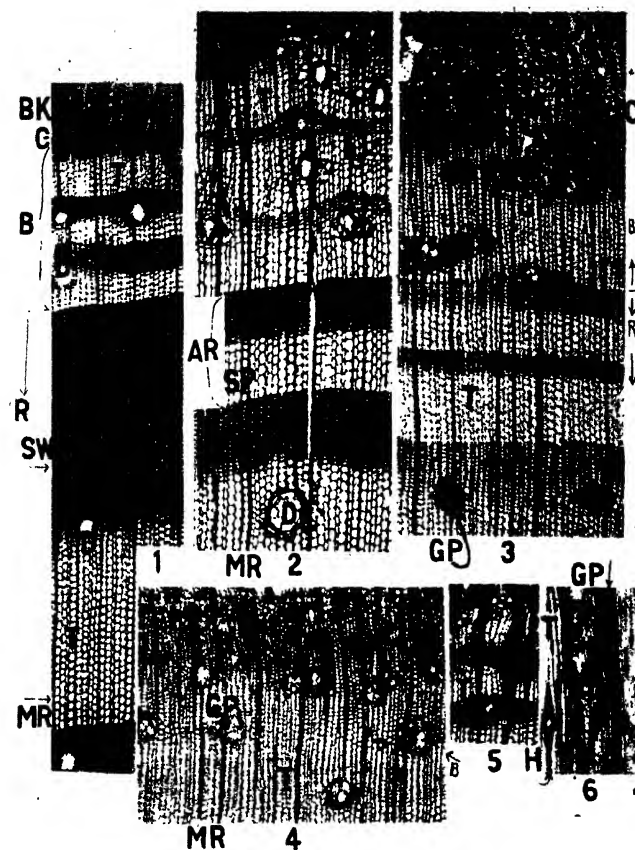


FIG. 22.

B, wood formed by "bled" timbers.

C, cambium.

D, gum duct or resin canal.

GP, group of "gum-" yielding parenchyma cells not opened to form a canal.

MR, rays.

AR, annual rings, one year's growth.

D and GP make up the vertical system of "gum-" yielding tissue.

H, horizontal resin duct, as seen on surface of face or in plain sawn lumber.

BK, bark.

R, wood formed in "round" timber.

SP, spring wood.

T, wood fibres or tracheids.

SW, summer wood.

1. A cross-section of a young fast-growing tree that was heavily turpentine-treated for three years. Note reduced width of annual rings in B, compared with growth

before turpentine R, also great reduction in the summer wood.

2. A tree also turpentine-treated for three years. Note more numerous but smaller ducts in B than in R (lower portion). Summer wood reduced here also.

3. A "virgin" operation with narrow chipping. Growth was not reduced in this tree; sample was cut in midsummer. Note abundant resin-producing cells, forming series (GP).

4. Similar to 3, but shows more clearly cambium, C, and the individual living "gum-" yielding parenchyma cells in groups or clusters GP.

5. Cross-section of new growth in spring wood. Only tracheids T have yet formed in new growth ring; no ducts yet present.

6. Lengthwise view of vertical "gum-" yielding system, GP, and end view of horizontal system at H.

single chipping a month before the regular turpentine season begins, and produces a much larger annual yield of oleoresin. It must be remembered that the production of turpentine is not the tapping of a storage reservoir. It must be carried on so as to husband the production of oleoresin and control the stimulation of the cells which produce it. The most successful flow of gum comes from the stimulated resin-yielding parenchyma cells, which are maintained in as normal a condition as possible with reference to such factors as moisture and food supply. For further details reference must be made to an article by Eloise Gerry on the *Production of Crude Gum by the Pine Tree*.⁹

A. W. Schorger¹⁰ finds that the oleoresin of heart wood of the Douglas fir has a $+2.84^{\circ} a_D$ and yields *l*-pinene ($a_D = -47.5^{\circ}$). He states that the photochemical processes occurring in the leaves and woody portion of certain conifers are different. The oil or essence from the leaves consists of closed ring compounds, chiefly terpenes in the case of *Pinus sabiniana* (digger pine) and *Pinus jeffreyi* (Jeffrey pine). From the woody portions of the tree aliphatic derivatives are obtained (normal heptane).

The oleoresin from *Pinus taeda* contains 15-30 per cent essence. Formerly it was collected according to the "box" system, wherein the exuded gum from "chipping" or "hacking" of the bark above the box was trapped (Fig. 23, left). The boxes are cut in the base of the tree about 10 in. from the ground. The box is a cavity, ranging in size from 10-14 in. in width, from 5-7 in. in the stump, and from $2\frac{1}{2}$ - $3\frac{1}{2}$ in. in the back according to the size of the timber. Each box holds about $\frac{1}{2}$ gall. of resin. The boxes are emptied six or eight times in the year, and 10,000 boxes yield by each dip forty casks dip-gum or soft gum, each of 240 lb. weight. The exudation of the resin is greatest in July and August. The collection is kept up for four to five years and then the tree is abandoned. This method of collection has been replaced by a cup and gutter system (Fig. 23, right), which preserves the life of the tree from four to eight years. By this method two shallow incisions and two galvanized iron strips (6-12 in. long and 2 in. broad) are placed at 120° to each other, and above a cup which collects the exuded resin.¹¹ Nevertheless, it is more wasteful than the French method.

The solid oleoresin left after the removal of the fluid part of what has solidified on the stem is removed by scraping (scrape), and is known as "gum thus" (the galipot of American turpentine).

A. Carey¹² states that the yield from the slash pine is much higher than from the long-leaf variety. The dip yield can be increased by moving up the cups annually.

H. Adams¹³ states that redistilled Jeffrey pine wood-turpentine gave 90 per cent normal heptane; and as the result of the examination of single-leaf nut pine, Jeffrey pine, and Western yellow pine, it was found that the turps oil from the wood and oleoresin are similar in character.

Tschirch and Hortschöner¹⁴ give the composition of the oleoresin

as containing parabietic acid, $C_{20}H_{30}O_2$ (sylvic acid of Fahrion), with an ethereal oil, a resene, and a bitter principle.

Venice Turpentine.—Venice turpentine is derived from *Pinus Larix*, the oleoresin of which is collected in spring, principally in Piedmont and in the Tyrol. It contains resin acids 60-64 per cent, essential oils 20-22 per cent, resenes 14-15 per cent, and various, 2-4 per cent.

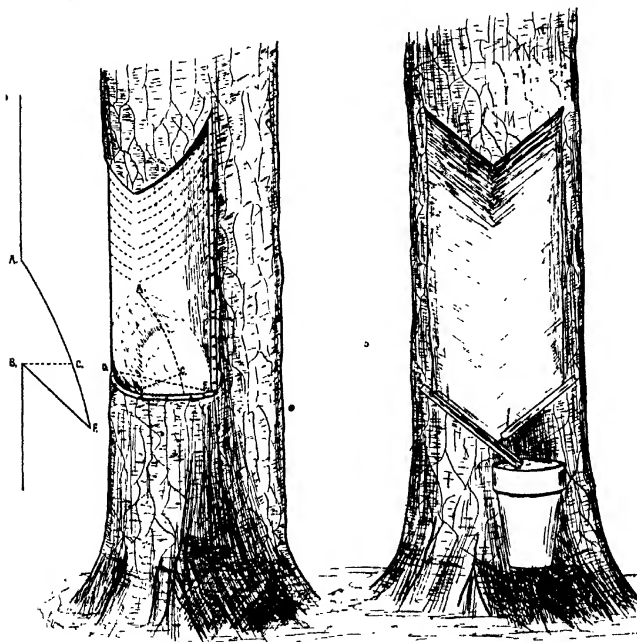


FIG. 23.—American collecting boxes. Left: Section and view of box system. Right: Cup and gutter system.

Andès¹⁵ states that by fusion of colophony in rosin oil and by addition of turpentine he obtained an artificial Venice turpentine.

Strasbourg Turpentine (*Pinus picea*).—Strasbourg turpentine solidifies by the action of magnesia, whereas Venice turpentine does not; this is of interest, because of the general coagulating influence of all alkaline earths on the depolymerisation products of the resins either in the form of rosin or of copal resins. It is collected twice annually (spring and autumn). It has a lemon-like odour. Its composition in amount of resin acids, oils, and resenes is nearly that of Venice turps.

Canada Balsam.—The collection of the balsam from *Abies*

canadensis is tedious. A tree yields on tapping not more than 8 oz., and the collection must be done in fine weather, otherwise the resin is cloudy. A tree flows only two years, and is then left three years. Even afterwards the yield is much smaller than in the first three years. The export from Montreal and Quebec is 20,000 kilos annually.

Tschirch and Bruning¹⁶ have isolated from the oleoresin the following acids :

Canadolic acid, $C_{19}H_{28}O_2$
 α and β Canadinolic acids, $C_{19}H_{34}O_2$ } soluble in sodium carbonate.
 Canadic acid, $C_{19}H_{34}O_2$ } soluble in ammonium carbonate.

The oleoresin contains resin acids, 63 per cent; essential oils, 23-24 per cent, b.p. 160°-70° C. and containing *l*-pinene, resenes 11-12 per cent, and various 1-2 per cent. Canada balsam is distinguished from other oleoresins by its refractive index (1.5194-1.5213 at 20° C.), so that a starch granule embedded therein remains visible, whereas in other balsams it is indistinct or disappears completely.

The general properties of the terebenthenes may be summarised as follows :

(1) The composition of the oleoresins of most varieties of pines is essentially the same.

(2) The essential oils are terpenes of different rotatory powers, acting as solvents of the resin acids, which are nearly of the same composition but differing in modifications.

(3) All may be made to yield a turpentine and a rosin.

Canada balsam, Venice and Strasbourg turpentine, are the most important oleoresins which are in general use.

Elemi.—This oleoresin is mentioned only for the purpose of showing the gradual transition from the balsam-like character to varnish resin, just as the following *Boswellia serrata* will be referred to to show the character of a gum resin in which the carbohydrate gum is associated with oleoresin components.

Elemi may be either balsam-like, as the oleoresin previously described, or passing to a solid resin form. It is generally too soft for oil-varnish resins, and finds use only in special spirit varnishes. It is stated that the films suffer on exposure to light and air. The most important varieties of elemi (obtained from the Burseracea family) are the Brazil, Mexican, Manila, and African forms. They are incompletely soluble in alcohol and turpentine, but soluble in a mixture of the two solvents. On distillation Elemi gives a mixture of dipentene and phellandrene.¹⁷ The resin contains 20-25 per cent amyrin (a mixture of two crystalline amyryns, $C_{30}H_{45}OH$), which is considered by some to be an alcohol (resinol), as it forms crystalline benzoates, by others as analogous to terpene hydrate. α -amyrin benzoate when distilled gives a hydrocarbon α -amyrene, $C_{30}H_{48}$, which forms a crystalline dibromide, m.p. 259° C.¹⁸ The composition of the two varieties of elemi is shown in the following table :

	Brazil Elem.	Manila Elem.
Amyrins, per cent . . .	30	20-25
Rosenes „ . . .	38	30-35
Acids „ . . .	25	13-19
Essential oils, per cent	20-25
Impurities, etc., per cent .	5-6	..

Indian Frankincense or Olibanum (*Boswellia serrata*).—This gum resin contains 55-57 per cent of resin, 8-9 per cent of turpentine-oil, and 20-23 per cent of gum, of which 74 per cent is soluble in water. It has been proposed as a source of turpentine and resin.¹⁹ Olibanum is a gum oleoresin (incense) from the Salai tree, coming from India and Africa. The exudation is known locally as salaigugl. Except as a source of rosin and turpentine it has no direct use in the varnish industry. The low acid and saponification values of the resin (51.6 and 61.3) make it useless for soap-making. The gum possesses weak adhesive power. The composition is of interest :

	Per cent.
Gum (carbohydrate) soluble in water . . .	30.8
Resin soluble in alcohol	56 (an acid $C_{20}H_{30}O_2$)
Essential oil	8
Insoluble	5.2

The essential oil on examination gives 81 per cent boiling below 160° C. and 14.4 per cent between 160° and 180° C.; + 4.54A₁; s.g. 0.8435 (Fowler and Malankar).¹⁹ The terpenes are stated to consist of pinene, dipentene, camphene, and p. cymene. The method of separation of the resin and gum consists in removal of the oil by steam distillation and hydration of the resin by heating with water under pressure, whereby the hydrated resin floats on the surface and can be removed as a solid on cooling. The gum forms a flocculent precipitate on the bottom of the vessel.

THE VARNISH RESINS

The resins are essentially exudations from trees (the direct vegetable origin of lac is disputed). About five-sevenths of the total imports of varnish resins into the United Kingdom are obtained from Imperial sources. In 1908 the imports were valued at £2,803,535; they included shellac from India, kauri from New Zealand, copal from British West Africa, animi from Zanzibar, copal and dammar from Singapore. Most of the Zanzibar copal is collected in what was formerly German East Africa, and a large part of the Singapore copal comes from the Dutch East India possessions. The varnish resins are more or less hard, friable or brittle, transparent or lustrous. They are insoluble in water (cf. *Boswellia serrata*); some are soluble in alcohol, ether, or benzol; others require strong fusion before they can be incorporated with solvents for varnishes. The researches of Tschirch and his pupils have thrown light on the composition of the resins, but fuller investigation is necessary, and a careful comparison of the components and of their decomposition products is very desirable. Generally the resins contain acids (resinolic acids, Tschirch); e.g. rosin

(colophony) contains abietic acid, amber contains succinoabietic acid, from which succinic acid can be isolated; dammar yields dammarolic acid, $C_{56}H_{80}O_8$, and dammarylic acid, $C_{36}H_{60}O_2$ (Franchimont); Zanzibar copal contains trachyloic acid, $(C_{56}H_{88}O_8)^*$.

Some acids are monobasic, others dibasic, etc., and oxyacids. No great reliance can be placed on the formulæ, as will be seen from the proposed formulæ for abietic acid given under colophony. There is always the uncertainty of complete purity of the acids analysed; moreover, in bodies of apparently high molecular weight the unavoidable analytical errors make it difficult to fix the number of carbon and hydrogen atoms with certainty. Important components are the resenes (Tschirch), which are oxygenated bodies, neither alcohols, esters, ketones, nor aldehydes. They are insoluble in alkalis, and their inertness renders their presence in resins of great importance in varnish making.

It has been suggested that the resene content is of value in estimating the quality of a varnish gum, but as dammar contains 62.5 per cent, Zanzibar only 6 per cent, and Manila copal 12 per cent, it cannot be said that there is much practical importance in the statement.

Dammar contains a resene, $C_{11}H_{17}O$ (m.p. $65^\circ C.$, sol. in alcohol), and β -resene (m.p. $200^\circ C.$, insol. in alcohol) as well as dammarolic acid, $C_{56}H_{80}O_8$, and a terpene, $(C_{10}H_{16})^{20}$

	Per cent.		Per cent.
Acid dammarolic	23.0	Water	2.5
α -resene	40.0	Ash, etc.	11.5
β -resene	22.5	Volatile matter	0.5

The resenes are stated to be derived from the oxidation of alcohols (resinols); they may be also of the nature of hydrates of the terpenes (terpineol). Dieterich states that fifty-three resenes are known.

The main constituents of the resins according to Tschirch are: resin esters, resin acids, resenes, and resinols.

Amber contains a succinoresinol, $C_{12}H_{20}O$ (m.p. $275^\circ C.$); pine resin, a pinoresinol, $C_{18}H_{18}O_6$ (also pimaric acid, $C_{14}H_{20}O_2$, and pimaric acid, $C_{20}H_{30}O_2$).

Elemi contains α - and β -amyrin, $C_{30}H_{46}OH$ (m.p. 183° – $184^\circ C.$ and 193° – $194^\circ C.$).²¹

Sumatra benzoin contains sumresinotannol, $C_{48}H_{18}O_3(OH)$, which yields picric acid with nitric acid and pyrocatechnic acid on alkali fusion. Yellow aceroides contains xantho-resinotannol, $C_{42}H_{46}O_{10}$ (Tschirch). Resinols have been separated from the softer oleoresins; cf. elemi, benzoin, turpentine.

The resinotannols which yield aromatic degradation products occur in the soft oleoresins such as benzoin, tolu balsam, and acaroid. The resinolic acids and the resenes are characteristic of the hard oleoresins and copals as well as of the soft oleoresins.

The Formation of Resins in the Plant.—The resin secretion cells of a plant may be stimulated by wounding to give a flow,

* Manila copal yields three monobasic acids, $C_{19}H_{18}O_2$, $C_{22}H_{34}O_4$, and $C_{25}H_{40}O_6$. (G. E. Richmond. *Philippine J. Sci.* 1910, 1, 177.)

and even if the plant shows no such secretion cells these can be generated, as in *Liquidambar* and *Styrax*, by destroying the new wood, whereby the flow of balsam can be continued for years, if the wound be enlarged from time to time. According to Wiesner, Möller, and others, nearly all the resins, gum resins, and balsams are formed in special secretory glands. The solid resins, such as those furnished by *Umbelliferae* (asafœtida, ammoniacum, etc.) are oxidised by the epithelial cells in the chizogenic glands, whilst the balsams are formed in the lysigenic oil cavities by dissolution of the cell membranes.²²

In the case of lac, Tschirch favours the view that it is partly vegetable and partly animal in origin. It is a special resin, containing a wax and colouring matter in addition to resin.

It is chiefly in connection with the oleoresin from the many species of pine that the production of resins in the plants has been systematically studied (see page 97). Many forms of copal are of fossil origin, whilst the softer varieties are collected by aborigines from living trees, but little attention is paid to improving the yield or extending the cultivation of the parent trees.

Classification of the Resins.—In view of the complexity of chemical composition, and in spite of the investigations of Tschirch and his pupils, it is difficult to classify resins satisfactorily, so that differences of chemical composition will go hand in hand with physical properties, which are apparently the more deciding factors of industrial importance. •

Tschirch in 1899 drew up the following scheme of classification :

(1) Resinotannol resins : (a) benzoic acid resins ; (b) umbellifer resins.

(2) Resene resins : (a) droseraceæ resins ; (b) dipterocarpeæ resins.

(3) Resinol resins.

(4) Resinol acid resins : (a) coniferæ resins ; (b) cæsalpinoideæ (hymenœa) resins.

(5) Gluco-resins.

Dieterich proposes the following classification :

(1) Resins which are esters of the aromatic series, either containing free acids or not : benzoin, dragon's blood, accroides.* These resins are soluble in methylated spirit. •

(2) Resins which are esters of specific resin acids, with or without free resin acids and containing essential oils, turpentine, mastic, elemi, etc. These are soluble or partly soluble in methylated spirit, or soluble in organic solvents. •

(3) Resins which are not esters, but contain only free resin acids, occasionally accompanied by inert admixtures (resenes) ; e.g. colophony, copals, sandarach, dammar, guaiacum.*

(The above schemes are of little practical value where it is essential to grade gums by their hardness, or more especially by the hardness of their films after sweating or running.)

Another classification is by age (balsams are excluded) :

(a) Recent resins, i.e. those which are obtained either from

* Holdt, Gardner and Jameson subdivide (3) into 3 groups based on the relative solubility of the unsaponifiable portion of the resins.²³

growing trees or from trees growing within recent times; this includes many of the copals and colophonium.

(b) Recent fossil resins: copals (certain varieties).

(c) Fossil resins; e.g. amber and the harder varieties of copals.

This scheme is not satisfactory, and is justified only by the experience that the older the gum the better it is considered to be.

Coffignier classifies the resins by a scale of hardness determined by a special machine: ²³

(1) Hard resins; (2) semi-hard resins; (3) soft resins; (4) special class, including amber, kauri, pontianac, and shellac; (5) various.

These are followed by the oleoresins (fluid and semi-fluid) and the fluid balsams.)

There is very considerable overlapping of each class in all schemes. It must be remembered that solubility is an important factor, and attempts have been made by Coffignier to connect this property with the practical value of the resins.

In varnish-making there are marked divisions between the oil varnish resins, the spirit varnish resins, and resins which are soluble in special solvents, but again there is overlapping. It may be stated with fair accuracy that the spirit varnish resins, with the exception of kauri (which is also soluble in alcohol), are not favourably accepted by varnish makers if linseed oil be used as medium (rosin wood oil mixings are now acceptable). The soft recent resins are generally completely or nearly completely soluble in methylated spirit; the oleoresins are generally soluble, likewise the balsams, except those containing true gum carbohydrate components. The copals are sparingly soluble with the exception of kauri. In general, sparing solubility in methylated spirit goes with age, as in the case of soft and hard manilas. For practical purposes the writer considers that this classification is simpler to follow, and prefers to grade the oil varnish resins according to the hardness of the oil films which they produce.

General Characteristics of Resins. Important characteristics of the resins are colour, hardness, lustre, and specific gravity. Some resins, e.g. mastic, occur in drop-like forms as the resin flows from the tree, others in short cylindrical pieces agglomerated together, as in sandarach, and others in large, irregular-shaped masses, as in copal gums. Lac appears in the stick form from the twig on which it has been produced by the lac insect. In the trade the resins often appear in artificial forms due to previous treatment in the country of origin; e.g. shellac in thin plates, dragon's blood in sticks. The surface of the resin is often characteristic; e.g. the weathering of the surface produces a goose-skin appearance, as shown in Zanzibar copal.

According to Wiesner, "Die Rohstoffe des Pflanzenreiches," not one of the plant resins is a chemical individual, but is a complex mixture. Mastic, sandarach, and dammar appear to be homogeneous; crystals are sometimes found in a matrix of resin, as in elemi, and abietic acid crystals in American turpentine oleoresin. The fracture of the harder resins is characteristic and conchoidal,

sometimes lustrous or dull; *e.g.* Zanzibar copal shows dull and lustrous alternations. Benzoin, yellow accroides, and others show almond structure with conglomerates of cloudy, rounded masses.

Colour.—The colour is very varied; from the colourless to red of dragon's blood, yellow of gamboge, and the black of some varieties of colophonium. Generally the colour is yellow to brown. The lustre is vitreous, but it may be waxy, as in the so-called almonds of benzoin. Some copals are entirely lustreless.

Relative Hardness.—According to Wiesner (*loc. cit.*) the hardness of the copal resins lies between gypsum and rocksalt, and a few, *e.g.* elemi, are so soft that they can be worked in the fingers. The softer varieties have naturally low melting points. Bottler, taking Zanzibar copal as the hardest, classifies copals in order of descending hardness: Zanzibar, Mozambique, Lindi, Red Angola, Pebble, Sierra Leone, Yellow Benguela, White Benguela, Cameroon, Congo, Manila, White Angola, Kauri, Sierra Leone (new), Hymenaea (Brazil).

Nicolardot and Coffignier²³ describe an apparatus for determining the relative hardness of resins by measuring the diameter of the impression made on a test block of the resin by a steel ball (2 mm. diam.) fixed on a 5 kg. weighted rod after 5 sec. and 10 min. contact at 0° C. and at 25° C. According to the measurements obtained, resins are classified as follows:

Hard resins: Zanzibar, Madagascar, Demerara.

Semi-hard resins: Congo, Benguela, Cameroon, Angola Red, Brazil, Angola White, Manila, Sierra Leone.

Soft: Pontianac, Dammar, Mastic, Sandarach, and Colophonium. Manila and Kauri vary according to the source.

The soft resins break under the weight of the 5 kg. charge.

Special class: Amber, Kauri, Manila, Pontianac, and Lac.

Other schemes have been suggested by Britton²⁴ and Parker;²⁵ and the latter has attempted to use the Shore "Scleroscope" Standard Test and finds that it picks out the very brittle resins, but is of little value in distinguishing medium and hard resins.

Solubility.—The importance of the solubility of the resins has been already referred to. Some resins are readily soluble in methylated spirit and are used in spirit varnishes, *viz.* shellac, sandarach, colophonium (rosin) and the softer varieties of copals. Others, such as dammar and mastic, are soluble in turpentine. Ether, benzene, and acetone are solvents for a number of resins. The copals are generally insoluble in vegetable oils until they are "run," but they will dissolve readily in the acids obtained from drying oils, although they are precipitated on addition of thinners. In petroleum they are insoluble or sparingly soluble, even when "run," so that addition of excess of petroleum thinners tends to render the resin in a resin-oil mixing very prone to separation. Terpeneol is also a solvent for a number of resins, also epichlorhydrin (Valenta).

The following table shows the solubilities of a number of resins obtained by Coffignier, who has determined the percentage of insoluble matter left after digestion of the resins with the solvents mentioned in the table:

	Turpen- tine.	Alco- hol.	Ether.	Benz- ole.	P. Ether.	Carbon Tetra- chlor- ide.	Aniline.
Zanzibar copal . . .	100	86	75	88	insol.	100	34.5
Red Angola . . .	77	37.6	51.2	70	"	77.4	2.3
White Angola . . .	69	15	27	50	"	61.3	3.5
Benguela . . .	69	16.5	43.7	65.6	"	74	0.9
Congo . . .	68	25	48	60	"	69	soluble
Cameroon . . .	78	67	59	72	"	74	8.4
Demerara . . .	92.5	72	55	40	"	75.5	74
Brazil . . .	18	30	30	40.5	"	45	8.3
Kauri (pale) . . .	77.5	6.6	62	67	"	81	soluble
" (brown) . . .	71	36	61	71	"	77.3	"
" (bush) . . .	73	12	55	62	"	77.3	"
" (collected) . . .	63	4	51	58	"	63	"
Manila (hard) . . .	73.2	56	58	64	"	69	"
" (soft) . . .	62	"	28.7	58	"	69	"
Pontianac . . .	66	"	46	63	"	62	"
Sierra Leone . . .	71	62	48	57	"	71	0.7
Dammar (Batavia) . . .	soluble	28.5	4	soluble	soluble	soluble	soluble
Mastic . . .	"	17	soluble	"	almost insol.	"	6.10
Sandarach . . .	74	soluble	"	67	partly sol.	79	soluble
Shellac (stick) . . .	89	11.9	83	83	"	88	2.2
" bleached . . .	91	3.6	77.5	80	insol.	90	soluble
Resin . . .	soluble	soluble	soluble	soluble	partly sol.	soluble	soluble
Amber . . .	83	86	81	79	insol.	89	69
Blendi . . .	"	"	soluble	"	"	"	"
Benzoin (Sumatra) . . .	"	21	"	"	"	"	"
" (Siam) . . .	"	4	partly sol.	insol.	partly sol.	"	"
Madagascar copal . . .	60	74	65	78	insol.	85	17.8
" fused . . .	4	92	52	15	partly sol.	"	"
After" naphthalene treatment . . .	52	75	20	40	partly sol.	"	"

It is only in a very few instances that insolubility tests can be considered as reliable for purposes of specification.

Melting Point.—On reference to the table given below it will be seen that for each resin there is a softening point and a melting point at which there is often decomposition. H. Wolff²⁸ gives a lower melting point at which the resin becomes transparent and a higher one at which the resin fuses completely in the capillary tube :

	Lower Melting Point.	Upper Melting Point.
	°C.	°C.
Shellac	90-100	115-120
Bleached shellac	60-70 if much water is present. Dried, shows same melting point as the unbleached variety	..
Accroides	80-100	150-180
Manila	85-125	110-180
Kauri	111	115-140
Brazil (hymenaea coubaril)	77	115
Cameroon (copaifera sp.)	96	110
Hard Angola	125	..
Zanzibar (fossil)	158	340-360
Lindi	143	340

It is evident that the melting points can only be approximate, because of the variation in composition of each variety of copal. It is natural that the younger the resin the lower the melting point. The melting points may be determined by usual or by special methods.²⁷

The "Drip" point is a rough melting point test in which the mass of the sample used is much greater than in true melting point determinations, and hence viscosity and surface tension of the melting material must be considered. It is of more value than the melting point, but the standardisation of test conditions is too difficult.

Acidity, Saponification Value and Iodine Value.—Although physical tests are of more value than chemical constants, the acidity of a resin is a factor to be considered in its behaviour in a gum mixing. In the sweating of a gum it will be noticed that there is often a lowering of the acidity. In the colloid mixing in which the resin is present a decrease in acidity is accompanied by a decrease in dispersion, and the fluid thickens or feeds up, consequent on the reduction of the acidity on sweating. In the table shown on page 122 it will be noticed that the harder fossil resins have a low acidity. The low acidity of kauri is noteworthy, and it is of great value in enamel paints, due to its non-feeding-up properties with pigments. The connection between acidity and the feeding-up of mixings has been much discussed, but it is considered that the acidity is not the only factor in the phenomenon.

Owing to the sparing solubility of resins in many solvents, the determination of the acidity has been under much discussion. Dieterich (*loc. cit.*) summarises the details of the methods up to the beginning of this century. (Offignier (*loc. cit.*) prefers to treat a solution of the resin obtained by extraction several times with 95 per cent alcohol hot, using a reflux condenser. The extract is filtered, and the acidity of the filtrate is determined and expressed in mgrms. KHO per gram of resin. The percentage of insoluble matter in absolute alcohol is also determined (page 122).

It is noticeable that some of the very sparingly soluble resins have a high acid value, indicating that the alcohol-soluble acids differ greatly in reacting weights. J. Marcusson and Winterfeld suggest the use of equal parts of benzol and absolute alcohol for extraction of the acids previous to titration. The writer favours this proposal, as the same method is of use in determination of the acidity of a varnish mixing whereby the end point of titration is clearly defined.²⁸ Direct titration of the cold solution should be used, but some materials demand back titration. In many cases it is desirable to use both, and some useful information frequently results from the double test.

The Saponification Value (Köttstorfer's Method).—This figure is obtained by half an hour's digestion of the resin with excess of standard alcoholic KHO. and is really the sum of the acid and saponification value, representing what is known as the Köttstorfer value. On comparison with the figures given in the table on

page, 122 it will be noticed that the ester content of the resins is small compared with their acid content.

Iodine Value.—The iodine values of the resins, as obtained by either the Hübl or Wijs method, are of importance in practice only in the analysis of shellac, which has a much lower value (16-17) than that of rosin (112-172), with which it is adulterated. A method of estimation of rosin in shellac is based on the iodine value (Langmuir). The values given in the table (page 122) indicate only the presence of unsaturated linkages in the resin ring and are not used for comparison of drying or oxidisable power, as in the case of the drying oils. The higher the iodine value the greater will be the tendency of the resin to become oxidised and to pass to a spirit-insoluble form, which may be of the nature of a resene. It is most probable that resenes are formed in the varnish film, as well as linoxyn, during the process of drying.

The statement by Parker²⁵ that Hübl's method gives better results than Wijs and Hanus is supported by McLean and Thomas,²⁹ who find that Wijs' solution causes a considerable amount of substitution.

Estimation of Resins in Mixtures.—The estimation of resins in a mixture by chemical methods is not conclusive. The iodine value, acidity, Köttstorfer values give indications, but the composition will be essentially speculative, and it is only in the special case of shellac with rosin (iodine value and Twitchell's method) that the results can be relied on. Stewart³⁰ put forward a method of estimation of mixtures of dammar and kauri. H. Ingle³¹ has devised a method for detecting and determining quantitatively kauri, manila, and dammar in admixture by means of the acid value and solubility in carbon disulphide. Kauri, manila, and dammar gums have acidities 50-70, 107-156, and 30-32 respectively, and on boiling each of the gums with a 5 per cent sodium carbonate solution, acidulating and weighing the precipitated acids, the yields were 6 per cent, 93 per cent, and 2.5 per cent respectively. Kauri and manila are completely soluble in benzol-alcohol (1:3), whilst dammar leaves 36-44 per cent insoluble, but is soluble in carbon disulphide. The analytical results obtained by Ingle from mixtures of known composition are quite satisfactory. Dieterich (*loc. cit.*) states that the following quantitative methods are applicable for the estimation of balsams, resins, and gum resins:

(a) Acid value; (b) saponification value; (c) percentage of moisture; (d) ash; (e) percentage soluble and insoluble in alcohol; (f) specific gravity; (g) percentage of solubility in other solvents.

Coffignier (*loc. cit.*), who has investigated the properties of resins for a number of years, states that the superficial examination by experts is rarely at fault and much of the resins used in varnish making are obtained on such recommendation. In the writer's opinion much is to be said for Coffignier's view, but cases have been known in which a closer attention to Dieterich's seven points given above would have avoided the occurrence of undesirable properties in special varnish mixings. It will not help the elucidation

tion of varnish problems if the resins are bought on superficial examination, so that in the mixings the special properties of the resin depending on chemical composition are ignored, which they cannot be. In a colloid mixing, variation in chemical composition, however slight, may have great effect on the resulting film, and the acidity of a resin may have a decided influence on the oil with which it is incorporated.

The ash content of a resin ought to be low; a West African copal may contain 0.2-2 per cent ash, manila 1 per cent, and kauri 0.5-5.5 per cent according to the grading. The loss in weight on "running" is given as more or less 25 per cent, but this figure cannot be relied on, because it is entirely dependent on the process employed. Some state that the desired conditions of incorporation with linseed oil may be obtained without loss in weight.³² The process is essentially one of depolymerisation, but the complexity of the resins must admit of partial decomposition of the component acids, with the liberation of volatile and fluid hydrocarbons (copal oil) and the formation of acidic anhydrides and lactones. References to the changes occurring during the sweating of the resin will be given in the next chapter.

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CHAPTER VII

OIL VARNISH RESINS

ADOPTING the simple classification given on p. 110 the copals appear in the class of oil varnish resins. They are recent or fossil, and are found in prehistoric forests or are dug out of the soil in what is still a forest region. The changes which have occurred in the secreted or exuded gums are not understood. Undoubtedly there has been reduction in acidity, with polymerisation or coagulation, and oxidation has occurred (the resenes are inactive oxides). It is unwise with our present knowledge to speculate as to the changes in such a complex mixture of colloid components. The recent copals, including manila, pontianac, etc., are not in demand by makers of high-class oil varnishes, but their softer varieties are soluble in methylated spirit. Rosin (colophony) is often a component of low-grade oil varnishes when rosin is cheaper than copal (as it usually is), especially in varnishes containing China wood oil. Among the oil varnish resins amber must be mentioned, although it is little used because of its price. The second class of varnish resins includes those soluble in methylated spirit—lac, sandarach, mastic, manila, copals (soft), rosin, and æcaroid resin. They are used for coatings, giving lustrous films of a brittle character (mastic is soft and elastic) and of comparatively slight durability for outside wear. Lac is undoubtedly the most valuable of this class, although mastic is used as a picture varnish, when dissolved in a suitable solvent. The third class includes many of the second class in addition to oil varnish resins which have been fused or “run.” The solvents employed may be turpentine, benzole, acetone, or coal-tar naphtha.

The above classification is only fairly satisfactory, but it is impossible to adopt any scheme based on differences in chemical composition, when in practice differences in physical properties are paramount.

The synthetic resins* belong to the second and third-classes. Few synthetic resins (*e.g.* albertol and cumarone resins) have been obtained which can be satisfactorily incorporated with oil. The resins obtained from phenols and their homologues by condensation with aldehydes and ketones are usually dissolved in methylated spirit when employed in varnishes. The cumarone and indene artificial resins and duroprene belong chiefly to the first and third classes respectively. At present, owing to their comparatively high price, they have only limited uses.

COPALS

These are essentially fossil, recent fossil, and recent resins. The term copal is a comparatively modern word, and according to Sabin is of Mexican origin, and said to signify any kind of resin exuding from trees. The earliest writer who mentions copal as an ingredient of varnishes is Fra Fortunato of Rovigo, between 1659 and 1711. Copal is now a generic term to include all varnish resins which are commonly incorporated with drying oils. The statement by Sabin that copal varnish is a trade name for a very inferior article made of common rosin is certainly not true in Europe, where it denotes rather a fossil gum-oil varnish. At present the bulk of the copal used in oil varnishes in this country is of fossil origin obtained from Central Africa (Congo), Zanzibar (Animi), West Africa (Angola), Manila and the East Indies (Manila), and New Zealand (Kauri). The supplies of fossil copal are limited, and sooner or later the softer copals obtained from the living trees will have to be utilised. It is stated that the supply of kauri copal will last only for forty years,¹ but W. E. Langguth² considers that there is as much gum in the ground as has yet been taken out, and that the available supplies are sufficient to last many years.

Kauri.—The resin is a fossil from *Dammara Australis* (*Agathis Australis*), a species of New Zealand pine. The gum obtained from the living trees is known as young kauri, and is softer and almost colourless. Young kauri trees when tapped yield the resin, and it is not uncommon to find deposits of resin in old trees. The occurrence and collection of kauri have been described in many text-books in considerable detail,³ as well as the statistics of the kauri gum industry and methods of separating kauri gum from extraneous material, also the kauri gum industry of New Zealand.⁴ A full account of the kauri gum industry of to-day is given by W. E. Langguth (*loc. cit.*), of which a brief abstract is given with a table showing the export of the gum.

The value per cwt. to England averaged 44s. 6d., whereas to America it was 69s. 9d. to 68s. 3d. The Americans buy the higher class of kauri.

It is estimated that *Agathis Australis* takes from 200 to 300 years to reach full maturity. There are few trees south of Auckland, although some pieces of gum have been collected in the South Island. The gum is of two types: (a) fossil, of which there is by far the largest quantity available; (b) that obtained by making incisions in the trees, called bled (or bush) gum. The size of the ground gum varies from lumps weighing 1 cwt. to that known in the trade as chips. Successive generations of trees have fallen on the top of one another and have thus formed deposits which often lie in strata. Gum is found as deep as 20 ft. below the surface, but generally at a depth of 4-8 ft. on hillsides and in basins. The basins are usually swamps, and in some districts are of a peaty nature. The gum digger knows where to find the kauri from his knowledge of the formation of the ground, and locates it by means

EXPORT OF KAURI FROM NEW ZEALAND
(1914 can be taken as a normal year)

	1914.	1917.	1919.
	Tons	Tons.	Tons.
United Kingdom	3335	620	346
Australia	19	11	..
Canada	70	1229	572
U.S.A.	4531	2689	1371
Austria	34
Germany	373	..	49 other
France	42	..	countries
Other countries	55	45	..
Total	8459	4594	2338

of a spear. A gum spear is a long, rectangular tapered ribbon of steel, 5 ft. long, with a handle similar to that of a spade fitted to the thick end. The spear is driven into the ground, and by the feel it can be ascertained if the point touches gum or not. In swamps the water is removed from the holes by pumping. The gum-bearing areas are bleak and sparsely populated. The kauri-bush or bled gum is obtained by making incisions in the bark of the tree, from whence the sap runs. The semi-plastic gum is allowed to harden in the sun, sheltered from the rain. The tree can only be bled for three years in succession, otherwise it is liable to die, and the quality of the gum deteriorates with each year's bleeding. Bush gum, although of good appearance, is immature and contains acids which make it unpopular with varnish makers. The fossil gum is washed and graded by hand by the exporter.

The principal factors which determine the value of kauri are colour, hardness, size, and cleanliness. The higher grades are used in the manufacture of varnish and paint, the poorer sorts for linoleum. Machinery is being used to replace manual labour, but the difficulties caused by the large number of trunks, limbs, and roots buried in the ground have not been overcome. The American varnish manufacturers state that there is no known satisfactory substitute for kauri, when it is desired to produce a high-grade and good-wearing varnish. In 1915 the New Zealand Government decided to enter the gum trade to maintain prices, but by injudicious buying on a large scale sent up prices too high. There is now some supervision of the tapping of the trees for bush gum, but its quantity is small compared with the fossil. Attempts are being made to face-dig certain swamp areas and to remove the surface of the soil and, in some places, practically all the soil; the material removed is passed through washing machines and the gum extracted. A considerable quantity of bold gum is being collected and the refuse distilled to give a kauri gum oil, which is being used as paint oil, leaving a residue of pitch.

East African Copals, Zanzibar Copal.—This copal (Animi) may

be taken as typical of the East African copals, which are derived from a species of *Trachylobium* occurring in Madagascar, in (formerly) German East Africa, and in Portuguese East Africa. It is said to occur in British East Africa. The fossil gum is found in sandy soil near the coast at a depth of about three feet. The resin-bearing trees also exist, and their mature fruits contain 15 per cent resin in the kernel and 8 per cent resin in the rind. The fossil copal has a peculiar goose-skin surface, and occurs in various sized pieces, but not in large masses like kauri. It is the hardest fossil copal and cannot be scratched by the nail, and has the highest melting point of any copal. Bottler found the melting point of some samples as high as 340°-360° C. Its solubility in solvents and other constants is given on pp. 110 and 122.

Madagascar Copal.—Madagascar copal is found as fossil and is also cultivated. The fossil is less hard than Zanzibar, and more decidedly coloured. Mozambique and Lindi are similar copals of about equal value.

West African Copals.—The West African copals (Angola and Congo) are probably derived from *Copaivera mopane*, which occurs in the great forests in the Congo basin. Red Angola is a fossil form found in the soil (four metres deep). Its surface resembles Zanzibar, but it occurs in much larger grains.

Benguela (Lisbon copal) is a resin difficult to fracture, coming to the market in characteristic lumps with deep indentations. It is of red to yellow colour, usually covered with a white opaque crust. The Congo resins have of late become popular among varnish makers, and a recent account of their occurrence and collection is of interest.⁵

Congo Copal.—In the Belgian Congo the copal is a secretion of *Copaifera Demeusii* and *Liquidamba styrflua*. The districts in which the copal is actively collected are essentially the tributary valleys of the left bank of the Congo between Stanleyville and Leopoldville. There are several varieties of copal according to where the copals are collected—*copal d'arbre*, *copal de forêt*, *copal de rivière*, and *copal d'eau*. *Copal d'arbre* is of medium value, being natural excrescences from tree wounds. *Copal de forêt* forms 80 per cent of the copal yield of the colony. The resin occurs in marshy districts comparable with the occurrence of kauri, but there is a considerable admixture (3-30 per cent) of mineral matter. The copal blocks (*pièces*) are found at depths of 5-90 cm., and are in demand by varnish makers. The collection is carried out by natives who camp out in the gum-bearing areas. The women and children use a sounding rod somewhat similar to that used by the kauri digger, but more primitive, and on the location of a lump it is extracted. The men provide the camp with food and do not dig.

The period of collection is from February to July, and begins when the soil has been sufficiently softened by a covering of water after the rains, which will allow the collector to walk half ankle-deep in the soft ground. A good collector can obtain 25-35 kilos

of resin per day, or 15-18 kilos on the average. The collected resin is dried in the sun and freed from earthy impurities by hand. The copal is bought from the natives either by the district authorities or by buyers visiting the camps, at prices which vary with the districts, or about 15-25 cents per kilo. The brokers sell at prices varying between 1250-2400 francs per ton (1250-1500 francs corresponds to 78s. per cwt in London, and 2400 francs corresponds to 5599 francs per ton at Antwerp). The cleaning of the resin is carried out at the dépôts, and the gum is packed in sacks of 45-75 kilos. In 1920 (nine months) 9,862,796 kilos were carried by the Congo Railway. In 1919 the export from the colony was 6231 tons. According to Coffignier the export of Belgian copal was 375,500 kilos in 1912, and 867,000 kilos in 1916.⁵

Copals from the Gold Coast Region.—In Southern Nigeria, the Gold Coast, and Ashanti, *Daniella oblonga* is the source of the resin, and in Sierra Leone and French Guinea, a species of *Cyanolhyrsus*. The supply of fossil gum is now very limited in this region, and all the copal resin from British W. Africa is obtained from living trees and is not a fossil gum. The forests run the danger of being depleted by wasteful tapping. In Sierra Leone the trees are tapped on a definite system, which consists in cutting out portions of the bark about 2-3 in. square, at intervals of about 9 in. on the surface of the stem and larger branches of the tree. The process resembles the tapping for rubber or turpentine oleoresin, but it is more difficult, because the rubber latex is secreted in lactiferous cells lying near the surface, whilst the resins are secreted in isolated vesicles in the bark or in resin ducts lying in the bark or in sap wood; moreover, the trees do not show such a "wound response" as in the case of the Para rubber tree, which gives a large increase of latex on second tapping. Restrictions are now placed on unsystematic tapping, and the Colonial Governments are endeavouring to increase the production of copal by planting trees and improving the yield of the resin.⁶

Accra gum is a fossil form from the Gold Coast.

Manila Copals.—The manila copal used by varnish makers is a generic term, having replaced the old commercial term, hard copal of the Indies. The varieties are numerous; some are comparatively hard, others soft. The hard manila is a fossil gum, the very soft manilas are collected from trees. The hardest variety comes from Borneo (Pontianac), and is superior to that obtained from Macassar. Java copal stands between Angola and Benguela in hardness and is superior to the Borneo resins. The oil of Pontianac and the other manilas is aromatic. The origin of the manila resin is *Dammara orientalis*, which is identical with *Agathis dammara*. It is cultivated in the Moluccas, New Zealand, especially in Java, as well as in the Philippines. The tree reaches a height of 45 metres and has a diameter of 2 metres. For obtaining the resin the tree is wounded by cutting long strips of bark from the stem, commencing 10-20 cm. from the ground, and the exuded resin, colourless and milky when fresh, becomes yellow or brown-

yellow and transparent when solid. A tree will bear for twenty-five years, and furnishes 250 kilos of resin. Around the tree the resin occurs as fossil in the ground, either in flakes or as compact blocks. The pieces collected are cleaned and graded into three varieties. The melting point increases with the age of gum and may rise to 120° C.⁷ The softer varieties of Manila copals are soluble in methylated spirit, whilst the harder varieties of East Asian copals are insoluble in turpentine or drying oils unless previously "run." They are still used by oil varnish makers, although they have not the popularity of the African copals and the New Zealand kauri. The Manila copals come to Europe through Amsterdam and Rotterdam. For a brief discussion of Manila copal and kauri resins as regards sources, botanical names, properties, and methods of production, reference may be made to an article on "Copals from the Dutch Indies," by M. K. Heyne.⁸

South American Copals.—These are obtained from the living trees, *Hymenaea coubaril* and *splendida*, of which the resin is yellow to yellow-red in colour. All the varieties, fossil or cultivated, are very soft and in small demand. M. Machenbaum⁹ gives the following comparison between Brazilian and Colombian copals :

	Brazilian Copal.	Colombian Copal.
Melting point . . .	127-160° C.	120-155° C.
Solubility in—		
Petrol-ether . . .	20	18
Ether	58	56
Alcohol	76	78
Benzol	33	38
Alcohol-ether . . .	92	92

Amber.—Amber is derived from *Pinus succinifera* (Goppert), and is found in blue earth beds in East Prussia in the Baltic region, where it is embedded in striped sand. Outside Europe amber is not found. Only one-tenth of the value of amber collected annually is used for varnish: in fact, it is little used by varnish makers, since the varnish films although very hard, are brittle and highly coloured because of the high fusion temperature and the difficulty of incorporation with drying oils. Its interest is mainly historical, and the derivation from a variety of *Pinus* points to the truth of the statement that any resin of a tree will in time under suitable conditions pass from a soft, spirit-soluble form to a hard, infusible, insoluble variety. The composition has been investigated by Tschirch, and the results have been referred to on p. 108.

Before passing to the consideration of the spirit varnish resins in detail, it may be advisable to summarise the properties of the oil varnish resins and to compare them with the spirit varnish resins in view of the overlapping of the classes.

The copal resins are graded according to hardness, colour,

fusibility, ash content, acidity, loss of weight on sweating, and solubility in drying oils to give a satisfactory varnish mixing. In practice the grading by the exporter is rather by size, hardness, and colour, while the varnish maker applies tests for the remaining properties. Much more reliance is placed on general experience in the selection of copals than on the values of the constants, which are given in the following table. Perusal of the figures will show the great variation in many of the values, so that they are of comparatively little use for identification purposes.

	Specific Gravity.	Per cent Insoluble Matter in Alcohol.	Acid Value.	Kottsdorfer Value	Iodine Value.
Copals :—					
Zanzibar . . .	1·058	83·8	60·123	75·92	79
„ fused	61	37	127
Madagascar . . .	1·056	92·6	48·78	66·83	..
Demerara	67·2	97	98·110	50·55
Benguela . . .	1·058	16·6	123·134	73·157	61·85
Angola (red) . . .	1·066	45·3	128	130·147	63·137
„ (white) . . .	1·055 (17° C.)	28·6	127	115·160	130
Accra . . .	1·033 (27° C.)	47·8	85·98	132	122·143
Cameroon . . .	1·052 (27° C.)	27	160	157	65·66
Kissel . . .	1·066 (27° C.)	19	70	118	..
Sierra Leone . . .	1·0645	62·3	110	115·130	63·138
Brazil . . .	1·053	20	123·149	132·153	123·134
Congo (hard) . . .	1·061	25·3	132	124·132	58·59
Kauri (brown) . . .	1·053	46	70·93	79	177
„ (bush)	12	51·83	83	..
Manila (hard) . . .	1·065 (17° C.)	3	72·136	87·215	90
„ (soft)	2	145	187	106
Amber . . .	1·080	74	97·140	115·154	62
Sandarach . . .	1·073	soluble	139·154	154·157	134
Mastic (tears) . . .	1·057	47·2	50·70	70·79	64
Dammar (Batavia) . . .	1·032	32	19·35	20·47	64
„ (Singapore) . . .	1·057 (18° C.)	20	30	39	123
Pontianac . . .	1·037 (16° C.)	soluble	134	186	119·142
Turpentine oleoresin . . .	0·856	..	70·164	157·210	143·6
Rosin . . .	1·07	..	145·185	168·176	116·257
Shellac (sticklac) . . .	1·009 (16° C.)	14·4	34·7	173·9	16·0

It is evident that all the resins in the table are heavier than water, with the exception of turpentine oleoresin, which yields turpentine on distillation. They have no definite melting point, which is to be expected, as in the heating there is depolymerisation of the resin, accompanied in many cases by decomposition, especially in the neighbourhood of high point of fusion. The soft resins have higher acid values than the harder varieties. The spirit-soluble resins have higher acid values than the insoluble varieties, with the exception of dammar and shellac. The Kottsdorfer gross saponification value is a measure of the ester content of the resin and is usually higher but never less than the acid value. The percentage of esters in manila is marked. The iodine value indicates the presence of unsaturated substances, and indicates the power

of the resin to be oxidised.* The very low value of shellac compared with rosin is of importance in the examination of the former for adulteration with the latter. The figures in the table are of more importance for spirit-soluble resins than for oil varnish resins. The oil varnish resins have to be sweated, and in doing so the chemical as well as the physical properties are profoundly modified.

The loss in weight in running varies with the character of resin, a bold gum losing less than "smalls" in the ordinary running pot. It may amount to (more or less) 25 per cent, but this figure cannot be relied on, because it is entirely dependent on the method employed for sweating or for depolymerisation of the resin. Some state that the desired conditions of incorporation with linseed oil can be obtained without loss in weight. The process is fully described in Coffignier's *Les Vernis*, p. 419. The principle is to depolymerise under pressure in the presence of an inert hydrocarbon, such as naphthalene, and to distil off the hydrocarbon, leaving the resin in an oil-soluble form. The method has not been universally adopted, for a number of reasons; it involves considerable special plant, and the process is much longer to carry out than the usual gum-running to be described under the Manufacture of Varnishes.

Properties of Sweated Gums.—The changes in properties in the following table refer to the sweating of gums in the ordinary way :¹⁰

Resin.	Raw.				Sweated at 300° C.			
	A.V.	S.V.	Per cent Unsap. Matter.	I.V.	A.V.	S.V.	Per cent Unsap. Matter.	I.V.
Sierra Leone . . .	72	119	18.8	106	13	115	17	125.5
Manila	127	175	16	138	68	136	23	133.3
Brazil	109	171	7.6	128	46.25	114	38.7	137
Kauri	37.4	54	20	91	17	61	10	67.7
Anilul 1	18.7	73	6.3	103	..	58.7	..	106
" 2.	30	32.7	76	127.5
Anilber	16.7	121.7	19	59
American Rosin . .	158	182	0.75	122	146	153	16	134
Shellac (dark) . .	61	203	3.6	36.5	11
Dammar	35	32.7	76	127	11	60	86.6	127
Sandarach (Mozador)	134	143	13.2	112	65	136	14.3	126
Mastic	52.7	83	51	175	23.2	50.2	49	165

It will be noted that there are variations in the values compared with those given in the earlier tables. These may be due to variations in samples themselves and also in the methods of determination of acid values, to which reference will be made. Coffignier uses the acid value determined by the acidity of the alcohol-soluble part.

F. H. Rhodes and H. E. Johnson¹¹ state that when copal resins are heated between 300°-390° C. there is a marked reduction in the acidity as determined by Worsfall's method, but no very appreciable change in the iodine value. The loss in weight is largely increased above 350° C. There is no connection between loss in weight on heating and the change in I.V. The experience of the writer is that if alcohol-benzol be used as a solvent in the deter-

* Manila copal when exposed to air rapidly absorbs oxygen, especially in sunlight, with the formation of peroxides. Carbon dioxide, formic acid, and hydrogen peroxide are also produced.¹²

mination of the acidity, the differences between the acid values of the run (oil-soluble) and unrun gum are often less marked, so that the apparent reduction in the acid value is no indication of the solubility of a sweated resin in linseed oil.

	Acidity before "Running."	Acidity after "Running."
Congo copal	93-94 (alcohol)	82-83
	95-99 (benzol-alcohol)	107

The following table gives the results of the determination of softening and fusion points of three copals, sweated and unsweated, as well as their acidities :

	Congo.	Manila.	Pontianac.
Softening point	212° C	200° C.	194° C.
Fusion " " " "	354° C.	289° C.	284° C.
	all with decomposition		
Softening point of the sweated resin	239° C.	257° C.	239° C.
Fusion point of sweated resin	248° C.	266° C.	266° C.
Temperature of sweating .	350° C.	300° C.	310° C.
Acidity "unrun" } alcohol	34	103	106
" "run" } method	20 (16% loss)	59 (23% loss)	70
but insol. in linseed oil	..	59 (no loss)	..

It is evident that the acidity varies only slightly with loss in weight, and that the proper solubility in oil is determined by the depolymerisation which occurs at certain temperatures which are peculiar to each resin. Kauri can be dissolved in hot linseed oil without previous sweating, and for that reason has been long preferred by many varnish makers.

It is to be feared that the values of the resin constants are of little use in attempts to fix the composition of a mixture of resins. They vary too much with the samples under examination, and no great confidence can be placed in the results. Only in the case of shellac adulterated with rosin are the iodine values admitted to be a gauge of adulteration, because of the wide differences between the values of the two resins.

Copal Oil.—The oil collected in the condensing systems dealing with varnish resin fumes has been investigated, but inadequately, by a number of chemists. Systems for the partial recovery of gum and oil fumes from varnish plants such as Tingary's, Andre's, Hackathorn's, Lehmann's, Neil's, and Koerting's, are described in books on varnish technology, and through their use considerable quantities of copal oils have been obtained. The oil has been used not only as a solvent for copal resins, but as a component of certain types of varnishes and paints. H. A. Gardner¹³ gives a list of the patents on fume recovery. Copal oil has been investigated by Tschirch and Niederstadt,¹⁴ who examined the essential oil (b.p. 156°-160° C.) from kauri bush copal, and by L. Schmoelling,¹⁵ who examined the copal oils from kauri and

Manila resins. He identified pinene in the distillate (b.p. 150°-160° C.) from kauri, but in the distillate (b.p. 60°-250° C.) from Manila he found neither limonene nor pinene. B. T. Brooks¹⁶ has investigated the destructive distillation products of Manila copal. The products obtained by distillation at 330° C., with 12-14 per cent loss in weight of the resin, included carbon dioxide 3.2 per cent, water 2.4 per cent, terpenes 1.5-11.2 per cent, and resin oil 3.6 per cent. Among the terpenes he identified pinene, β -pinene, camphene, dipentene, and limonene. Between 320°-360° C. large quantities of copal oil were distilled from the resin. He pointed out the influence of the copal oil in assisting the solution of the resin in linseed oil. G. Grassner¹⁷ has also investigated the products of the destructive distillation of the copal resins. The writer has examined, but inadequately, the condensed fumes from the sweating of Manila and Congo copals under works conditions of running and condensation. The fumes were found to contain 5-10 per cent of terpene, volatile in steam, which consisted of a mixture of terpenes similar to that obtained by Brooks. The terpenes gave 50 per cent distillate at 170° C. and 87 per cent up to 185° C. On distillation of the fumes under reduced pressure (20 mm.) the heavier copal oils could be roughly fractionated; e.g. 20 per cent (s.g. 0.909) boiled over between 125°-150° C.; 18 per cent (s.g. 0.929) between 150°-175° C.; 20.1 per cent (s.g. 0.947) between 175°-208° C., leaving 37.6 per cent semi-solid residue. The heavier copal oil distillate contains a mixture of sesquiterpenes (cf. caryophyllene, $C_{15}H_{24}$, from copaiba balsam), or polyterpenes (cf. colophene, $C_{20}H_{32}$, from the polymerisation of turpentine) with volatile acids. The non-volatile residue (A.V. 59-71) resembles in its properties a soft resin in that it will dry hard on exposure to air, will form metallic dryers, and generally act as a resin component in a linseed oil varnish. The acid value of the fumes obtained from Congo copal was 59, so that the acidity of the fumes is confined essentially to the less volatile components. In connection with the solvent properties of the fumes already referred to, it is of interest to note their strong solvent action on rubber. It must be admitted that the published literature on this important subject is very scanty, and the copal oils, together with the volatile acids, are worthy of fuller investigation.

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CHAPTER VIII

SPIRIT VARNISH RESINS

THE second class of resins includes dammar, mastic, sandarach, acaroid, lac (shellac), rosin (colophonium), and the softer varieties of oil varnish resins which have been described in the last chapter.

Dammar.—This resin is a typical exudation from *Dammar orientalis*, indigenous to the Dutch East Indies and British Malaya. Under this name a large number of varieties (more or less soft) are included. Dammar comes into the market generally in the form of nodules, clear and pale in colour. It is decidedly softer than the majority of copals, but it is harder than rosin. The resin dries with a tack, and as a spirit varnish gives a friable coat, which can be easily rubbed up into a powder. The most important trade varieties are: Batavian dammar, Singapore dammar, pontianac dammar (from Borneo), which is whiter than the Singapore variety, pale Borneo, Sumatra, and Padang (Sumatra) dammar. *Dammar Australis* is the kauri tree of New Zealand, and gives the cultivated soft kauri already described. Black dammar is obtained from incisions in *Canarium strictum* of India (also called Kala dammar).

Dammar is soluble in turpentine in the proportions of 3.5 : 7.5, and the solution dries in five to nine hours. It imparts lustre to films and is harder and better than rosin, but not so durable as an oil varnish resin (see later under Crystal Varnishes). Its very pale colour compared with other varnish resins makes it a component of varnishes where colour has to be considered.

Mastic.—This resin is the most important European form known with the exception of rosin and amber. It occurs in the Mediterranean littoral, being obtained from *Pistachia lentiscus*. Much comes from Greece and its islands, especially Chios, either as cake, large or small mastic. The *Pistachia* has a marked wound response, so that under good conditions a tree may yield 10-18 lb. per annum. The smell of the resin is feebly balsamic, and it has a slightly bitter taste. Varnishes containing it are only slightly coloured, and are satisfactorily elastic. It is used in turpentine solution in picture varnishes, and with boiled linseed oil forms megilp, the well-known artists' medium. Its melting point is

103°-108° C. The present practice of protecting pictures by an easily removable mastic varnish is justified.

Sandarach.—Sandarach is a North African resin, being the exudation of *Callitris quadrivalvis*, which tree grows also in N. America. *Callitris calcarata* and *glauca* in Australia also yield sandarach. It is comparatively hard, and is used to impart that property to other resins. It is said by some to be as hard as kauri and superior to mastic, which it scratches. It is an ingredient of negative varnishes, label varnishes, and bookbinders' varnishes. It is soluble in methylated spirit and in ether, but only slightly soluble in turpentine, benzole, and petrol.

Acaroid Resin (*Gum Accroides*).—*Xanthorrhœa* or grass tree (*Asphodelaceæ*) is confined to Australia and Tasmania. It is a plant with a short woody stem terminated by a tuft of long leaves (about three feet) with cutting edges. The three most important species are *X. hastilis* (yellow acaroid gum), *X. arborea*, and *X. Australis* (grass tree gum, red gum acaroid). From the trunk of the tree on incision flows a resinous substance giving a layer 2-4 cm. thick of resin in the case of *X. hastilis*. Sometimes fragments detach themselves and collect at the foot of the tree, where they are found buried and semi-fossilised. *X. hastilis* (Botany Bay gum) yields a yellow resin of the composition: matter soluble in alcohol 82.7 per cent, insoluble in alcohol 13 to 14 per cent; moisture 3 per cent; ash 1 to 3 per cent (matter insoluble in ether 23 per cent). The melting point of the resin is 97° C. The red resin (red yacca gum) obtained from *X. arborea* and *X. Australis* has the composition: matter insoluble in alcohol 4 per cent; matter insoluble in ether 16 per cent; moisture 3.5 per cent; ash 0.24 per cent. Its melting point is 110° C. A sample of the red resin, purified by extraction with alcohol, yielded 2 per cent free and combined para-cumaric acid, 0.1 per cent cinnamic acid, 0.1 per cent styracine, traces of aldehydes, and a residue of phenolic compounds. Distillation of the resin yielded 17 per cent of an oily distillate of a phenolic nature. Oxidation by nitric acid yields about 30 per cent picric acid from the yellow variety and 25 per cent from the red variety.¹ Red gum acaroid approximates to dragon's blood in colour, with a shade approaching brown, possessing an orange streak. In lustre it is superior to the above-mentioned resin. Both varieties are soluble in alcohol and alkalies, but insoluble in petroleum ether, and in this respect resemble shellac. *Xanthorrhœa* resins belong to the same class as Peru balsam, storax, and benzoin. During the Great War it was suggested that they might be a source of picric acid. *Xanthorrhœa* resin is also obtained from Kangaroo Island and W. Australia. By steam distillation of a strongly alkaline solution, pæonal (2-hydroxy-4-methylacetophenone), hydroxypæonal, l-citonellal, and probably methoxydiphenylether have been obtained.² Recent patents have been taken out by H. C. Miller and H. A. Ireland in connection with acaroid resin.³ Details as to its use in spirit varnishes will be given in another chapter.

LAC *

The most important of the spirit-soluble resins is Lac, which possesses a degree of elasticity, hardness, and power of adhesion to smooth wood and metal surfaces, distinguishing it from other resins. Lac comes into the market in various forms, such as grain lac, flake shellac, button lac, garnet lac, bleached shellac. The original resin is the secretion of the lac insect (*Tachardia lacca*), which is found on a number of species of Indian trees, e.g. acacia, ficus, mimosa, etc.; the most important of which are the Kusum (*Schleichera trijuga*), which yields the best shellac; the Ber (*Zizyphus Jujuba*), which is becoming more popular, as it is easy to cultivate; the Ghort (*Zizyphus xylopyrus*); and the Palas or Dhak (*Butea frondosa*), which is a common tree and often preferred. These trees contain much gummy or resinous matter or are rich in latex. The lac insect belongs to the group of Coccidæ or scale insects, the scale being an exudation of amber resinous material or lac, which envelops and cements them together to form a coating around the twig of the tree upon the juices of which they feed. The female lives for about six months, producing eggs in the cavities in the lac, from which emerge eventually a swarm of very slow-moving crimson or violet specks which travel along until they find a suitable branch to which they can attach themselves and carry on their functions. There are two broods or swarms in each year and two crops of lac, winter and summer crops. The female insects remain embedded in the lac for the whole period of their lives, but the male insect, which is smaller and produces much less lac than the female, crawls out during the pairing season and visits the female. The males of the summer brood are stated to be wingless, but those of the winter brood are provided with wings. The crop of lac varies considerably from year to year, owing to the effect of climatic conditions on the insects. The most favourable situations where the lac is most abundantly grown, i.e. Chota Nagpur, Orissa, and the North-East of the Central Provinces, are generally 1000 ft. above sea-level and possess a fairly temperate climate with an annual rainfall of 50-60 in., occasional showers falling at times other than the regular rainy season. A considerable amount of research has been carried out on the history of the parasites which attack the lac insect, but the Report of H. A. Lindsay and C. M. Harlow⁴ emphasises the paucity of knowledge on the biological side of the lac insect, its food-plant, and the need for much more extended observation. The food-trees, distribution, and cultivation are all discussed, as well as suggestions for improved methods of cultivation and storage, etc. For a complete description of the native method of preparing shellac, reference may be made to the report, which is well illustrated by drawings; e.g. the coolie woman grinding and sifting the lac, the Ghasandar washing lac in bowls, the Karigar melting the lac over the fire, and the Bhilwaya stretching the lac with hands and feet

* Sanskrit *Laksha* (Hindi *Lakh*), a hundred thousand.

into large sheets, which are broken up into scales of flake lac. A few firms manufacture shellac by machinery, the lac being dissolved out with alcohol and the latter evaporated off, the lac being then run out in the molten state and converted into the button form. This shellac differs from that made by the native method, being darker and probably more affected by heat; moreover, it is less soluble. At present it is doubtful whether mechanically-made shellac is as suitable for all purposes as that made by native methods.

The history of the lac industry is ancient. Previous to its employment in varnishes and polishes, lac was used for dyeing, the red colouring matter being extracted and used for that purpose and also in the preparation of crimson lake. The residue was thrown away. Subsequently the residue was worked up into shellac and became the most important product when the introduction of aniline colours stopped the export of the lac dye in 1888-9.

In 1888-9 the value of the export of shellac was 3,200,000 rupees.

" 1899	"	"	"	7,000,000	"
" 1908-9	"	"	"	25,000,000	"

The imports of shellac, of which 95 per cent is produced in India, into different countries is given in the following table :

	1912 (Cases).	1919 (Cases).
U.S.A.	111,000	139,000 (each containing 2 maunds - 1½ cwt.)
United Kingdom	50,000	56,000
Germany, Holland, and Austria	63,000	450
France	16,500	5,450
Japan (through U.S.A.)	600

The price of shellac varies in the inverse ratio with the stocks in London. At the outbreak of the Great War the stocks were very high, but in December 1916 the stock was reduced to nearly half and the price was more than doubled. The Government put on a control and obtained a fixed delivery price, which caused prices in London to rise sevenfold above the pre-war rate, to 450s. per cwt. Prices dropped to 205s. per cwt. in April 1919, only to rise to 880s. in January 1920 since then the prices have dropped.

The principal defects from which the lac industry suffers at present are speculation and adulteration. Both have their origin in the peculiar conditions of the industry; the ignorance and improvidence of the cultivator; the long distances the stick lac has to be brought to the markets; the large number of agents through whose hands it passes; and the difficulty of estimating forthcoming supplies. The commonest forms of adulteration are sand and ashes in grain lac (seed lac) and rosin; this can be controlled analytically by use of Parry's method (London) and Langmuir's method (New York). Formerly there was considerable local prejudice against

the manufacture of shellac. There is still current a proverb, "Sau kasahi ek lahi": "one lac manufacturer is as bad as 100 butchers," referring to the destruction of insect life caused by the collection and manufacture of lac.

Improved methods of cultivation on intensive lines in Government forests by Provincial Forest Departments are recommended, with a careful selection of the host trees. The greatest importance is attached to the organisation of brood and demonstration farms so as to assure constant supplies of brood lac of good quality. Moreover, cultivators must learn scientific methods of cultivation and collection, with the organisation of co-operative credit societies for the maintenance and distribution of supplies of brood lac, and the formation of Research Associations to be supported by the Lac Trades Association. The Special Committee of the Imperial Institute to consider the trade in lac suggest:

(1) That the method of leasing concessions to collect lac should be improved and systematised after an inquiry in India; longer periods of leases and a sliding scale of royalties are proposed.

(2) That greater attention be paid to improved methods of cultivation and collection of lac, and an advisory and supervisory agency should be constituted.

(3) That one or two large-scale Government factories be started, to put the manufacture on a thoroughly efficient basis and safeguard the interests of India and the Empire; lac-ware manufactures to be encouraged in India.

(4) That definite marks and grades be established, in consultation with the Imperial Institute, to ensure the maintenance of standards of purity and quality.

(5) That the system of trading be simplified, and more direct relation established between the Indian producer and the British user.⁵

Industrial Uses of Lac Resin.—Lac resin is one of the most important resins of commerce, and owes this position partly to properties (such as high resistance to the action of air and moisture, adhesiveness, and high electrical resistance) which it shares with all resins, but chiefly to the fact that its ready solubility in alcohol renders it easy of application. There is no satisfactory substitute for lac resin among natural resins, and the synthetic production of shellac is a competitor only in certain special requirements. The principal uses of lac resin are:

(1) As an electrical insulating agent, chiefly for special insulators having paper or mica (micanite) as a basis, and for insulating varnishes.

(2) As a stiffening material for felt, straw, etc., for hats, and for crêpe.

(3) As a preservative coating for wood and metal in the form of varnishes (spirit- and water-soluble) and lacquers. For these purposes it is employed in a great variety of industries, and especially during the war in the protection of shell parts.

(4) As an adhesive material in special cements, sealing-wax, gramophone records, etc.



Lac resin must be regarded as an important war material, and from this point of view it is essential that its production should be safeguarded, and that there should always be an ample stock in the United Kingdom.

Manufacture of Shellac.—The full details of the manufacture can be obtained from the Report, of which a very brief summary will be given here.

The object of the manufacture is to refine the crude lac and remove the dye, fibre, animal remains, and other impurities. The first step is to clean the stick lac and remove the woody matter. The best method of collection is to break off, by a twisting movement only, the resinous incrustation after the insects have swarmed. It is then ground and winnowed to complete the separation of the lac and refuse. The seed-lac is specially washed with water and dilute sodium carbonate to remove the dye, finally with water, and dried on a cement floor (grain lac seed). The dye extracted in the washing was originally the staple product of the industry, and it is prized for its bright scarlet shade. It was used to dye the British infantryman's tunic (like the madder for the French poilu's trousers). The word lake in crimson lake is derived from lac, and the word crimson from the Arabic (kirmez = insects), from which Kiri (Urur) is directly derived. Kiri is the animal refuse from the bags from which the lac is expressed. To the grain lac is added a little orpiment (yellow arsenic sulphide), to give the trade colour requirements, which is followed by an addition of rosin (3 per cent). The grain lac is now transferred to a roll of cotton, and the roll containing the grain lac is gradually warmed by bringing it near a fire; the ends of the roll are squeezed so as to drive the molten shellac through the cotton, leaving the kiri (animal refuse in the roll). The molten shellac is allowed to solidify on plates or water-cooled rolls, from which it is removed in flakes, of an orange-brown colour, constituting the flake lac of commerce. It would appear as if the manual process has hit off by sheer accident the proportions of resin and wax which produce the best quality of shellac known. The machinery processes are at present expensive, and if the supply of stick lac is short the machines cannot work regularly and capital charges are high. The yield of shellac per Bengal maund (82 lb.) of the Kusmi ari (lac collected before the insect swarms and containing insect and dye) is 32-33 seers (1 maund = 40 seers). Kusmi grain-lac gives 36 seers shellac per maund.

Grades of Shellac.—Shellac is a complex mixture of resin acids, resin esters, and a wax. The resin acids are probably derived from hydroxyfatty acids.⁶ Shellac is a derivative of aleuritic acid, probably as an ester of the acid $\text{CH}_2\text{CH}_2\text{CH}_2\text{CHOH}(\text{CH}_2)_7\text{CHOH}\cdot\text{COOH}$.⁷ C. Harries and W. Nagel⁸ state that aleuritic acid is trihydroxypalmitic acid and comprises 30 per cent of ether-insoluble part of shellac. Stick lac contains 66 per cent resin, 6 per cent wax, 6 per cent gluten, and 11 per cent colouring matter.

¹The best lac is produced from the Kusum tree!

The bulk of the shellac manufactured is  (probably the mark of Talpam Naturam (a manufacturer of Belapur) or Triloki Nath, Bengali. It contains no rosin, and is of the flake lac variety. Calcutta brokers blend 12 per cent rosin-shellac with T.N. to make a 3 per cent mixture, which is standard in London. Machine-made shellac is not accepted as  brand.

The added rosin is stated to be always Canadian rosin and not Indian, which has not as yet proved satisfactory. Rosinous shellac is always sold as shellac, and, in view of the trade requirement, the rosin can hardly be looked upon as an adulterant, although its amount must be controlled.

Shellac when applied to a warm metal surface gives a hard, lustrous film which is a valuable protective indoors coating. In a damp atmosphere it disintegrates and the film becomes rough and powdery, and does not regain its original condition on the expulsion of the moisture. As a hard priming coat on wood it is very satisfactory, especially if the woodwork contains knots, but it is stated that it is inadvisable to prime knots with shellac previous to the application of paint.⁹ Its electrical insulating properties are very good. By far the largest demand for shellac is in the manufacture of gramophone records.

Shellac is soluble in aqueous solutions of alkalis, alkaline carbonates, and borax; this property is utilised in the preparation of shellac water-varnishes and in the production of a bleached shellac soluble or partially soluble in alcohol.

Bleached Shellac.—Weak alkaline solutions partially remove the colouring matter from crude shellac. To bleach shellac it may be dissolved in alkalis and chlorine passed in. Ten parts shellac are dissolved in two hundred parts of water containing one and a half parts sodium carbonate, and chlorine gas, diluted with ten times its volume of air, steam, or any other indifferent gas, is passed in for twenty-four hours. The precipitated lac is collected, melted under water, and when soft is pulled out so as to give it a fibrous, satin-like appearance. Shellac may be also bleached by dissolving it in a solution of sodium carbonate and adding gradually a solution of sodium hypochlorite. The loss in weight of the lac in the process is about four per cent. The bleached lac is perfectly white, but it is more friable than shellac. It should be kept under water to prevent it losing its solubility in spirit, and even under these conditions it gradually deteriorates. The spirit-soluble form is the component of the so-called transparent lacquers. Bleached shellac is seldom completely soluble in methylated spirit.

A lac water-varnish is a water solution of shellac or bleached shellac in borax; it makes a good waterproof paper varnish. (See further under Shellac Varnishes.)

Button Lac.—This variety is sold at a lower price than shellac of the same grade, as it does not go through the process of stretching

and hence the cost of manufacture is less. It is obtained in the form of large, flat or slightly hollowed buttons by stirring the crude lac with hot water for several hours to remove the colouring matter, melting, and casting into buttons. It is not so popular, because it has generally to be ground before use. It may contain rosin up to 20 per cent, and such admixture is made to facilitate melting during manufacture (Lindsay and Harlow, *loc. cit.*). The best varieties are pale in colour and free from rosin.

Garnet Lac.—Garnet lac is a special preparation of shellac characterised by being free from contained wax. The waxy constituent of shellac being insoluble in alcohol, a clear solution is not obtainable from any variety but garnet lac. It usually contains 10-20 per cent of rosin and has also to be ground before use.

Shellac, freed from the wax (m.p. 58°-59° C.), is obtained by either fractionally precipitating the wax from a strong alcoholic solution by water, the wax separating out first and the shellac remaining in solution being recovered by distillation of the alcohol, or by treatment with an aqueous solution of alkali carbonate, wherein the shellac dissolves, leaving the wax insoluble as a scum. In the latter method the shellac is recovered by acidifying the alkaline solution.

As is well known, shellac on storage gradually becomes less soluble in alcohol, and it is said that by soaking in water for some days its solubility is improved. Seed lac becomes less soluble more rapidly than shellac, and shellac more rapidly than button lac. T.N. shellac loses 5 per cent solubility per annum during the first three years.

D. Hooper¹⁰ gives analyses of the four most important varieties of crude lac, of which Kusum may be quoted: water 1.8, resins 85.6, colouring matter 2.5, residue 9.1, ash 1.0; total 100. Shellac from Kusum lac has an acid number 61.1, saponification value 201, iodine value 9.6, insoluble in alcohol 0.7 per cent. Rudling¹¹ examined three samples of shellac and gives the following figures:

	Water.	Insoluble in Alcohol	Acid Value.	Saponification Value.	Iodine Value.
Stick lac . . .	3.79	14.4	39.2	213	16.0
Seed lac . . .	2.63	11.7	53	218	7.5
Button lac . . .	2.0	3.1	59	204	22.2

The varieties melt between 77° C. and 82° C., the button and garnet lacs having lower melting points than stick lac. Further references to the literature are given at the end of the chapter.¹²

ROSIN. COLOPHONY. COLOPHONIUM

Under the oleoresins it has been shown that on distillation the residue after the expulsion of the turpentine spirit is rosin, which

in turn on further distillation under different conditions yields a volatile rosin oil and a residue of rosin pitch. The properties of the spirits of turpentine will be discussed later, whilst those of rosin fall under the heading of spirit-soluble resins.

The "gemme" of Bordeaux oleoresin, which has a disagreeable odour and an acid and bitter taste, is in its raw state a thick transparent liquid which subsequently becomes cloudy and viscous. Its average composition is: Oil of turpentine, 15-20 per cent; dry products, 70-80 per cent; water, 10 per cent; sand and impurities, 2 per cent.

French Method.—The first stage in the *térébenthinage* (recovery of turpentine) is the purification of the gemme by the separation of the sand, wood rubbish, and water. On arrival at the factory the gemme is next distilled by a special process which will be

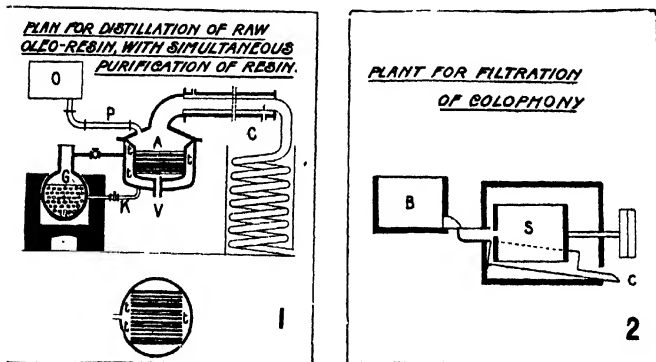


FIG. 24.—Distillation of oleoresin and filtration of colophony.

referred to under the Manufacture of Turpentine. The plant for the distillation of raw oleoresin (Fig. 24, 1) consists of a steam generator G, a still A, and a condensation apparatus C. The generator does not possess any special characteristic, but the still is made entirely of steel and capable of supporting a pressure of ten atmospheres. Its cover is provided with a tube P, for the introduction of the gemme coming from the reservoir O, and a still head which conducts the turpentine vapours into the condenser C. The lower part of the still is provided with a pipe V, by which the rosin escapes. The actual boiler is prismatic in shape and traversed by tubes *t*, which are arranged like a grating and connected with the steam jacket which surrounds the whole. The water condensed in the jacket is conducted back to the generator by the tube K. The gemme, thus exposed to the heat from the tubes, which present a very large heating surface, is very readily separated and distilled. During the distillation an injection of water is made by means of a cap placed in the dome. The solid body left in the retort,

more or less coloured and having an acid reaction, is colophony. It still contains a little water and nearly always solid impurities. In order to remove them the temperature is raised until the last traces of water are expelled, and the molten rosin is passed through sieves or filters to get rid of the solid impurities. In the filtration of the rosin, steam under pressure is made to act on it in a resistance boiler, heated externally by a steam jacket, whilst the bottom of the boiler is pierced with holes covered by material to retain the impurities, or alternatively the melted resin passes from B (Fig. 24, 2) into a hollow revolving cylinder S, the walls of which are made of suitable filtering material (metallic cloth), whereby the solid impurities do not interfere with the filtration due to the rotatory movement. The colophony is received in a receptacle and comes out at C, perfectly clear and free from all impurities. It is collected directly in moulds, and the loaves obtained can be packed and delivered direct for immediate use.

American Method.—In the American method, stills holding 800 galls. (20-25 casks) of oleoresin are fire-heated to fuse the oleoresin and a thin stream of lukewarm water is added to the charge during the heating. The water and the oil are collected, and the molten resin left in the still is graded.¹³

Properties of Rosin.—The best grade of French resin (window glass or *verre-à-vitre*) is purified rosin, bleached in the sunlight by exposure of the loaves for two weeks or by ultra-violet rays from mercury lamps. If the rosin has been properly prepared it is clear and of a pale amber colour. Common rosin is of a darker colour. Black rosin is opaque and very dark, and is found at the bottom of the fusion pots in the distillation of the oleoresin.

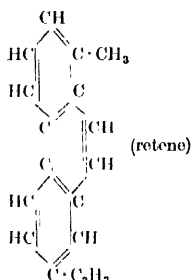
The American grades are :

W.W., water-white; W.G., window glass from "virgin dip"; N., extra pale; M., pale; K., low pale; J., good; H., No. 1; F., Good No. 2; E., No. 2 D., good strain; C., strain; B., common strain; A., black.

The specific gravity of colophony lies between 1.070 and 1.080. It melts at 120°-135° C. with an acid value of 168-171.5, and a Köttstorfer value of 168-174. It is soluble in most solvents except water, but it is volatile without decomposition in steam under reduced pressure.

Rosin does not alone form soaps of practical utility, but it is a valuable ingredient of a soap fat stock, endowing the finished product with a polish and lustre together with that odour which is favoured in household soaps. Lump rosin is superior to powdered rosin in soap-making power. Rosin soap is not readily precipitated from its aqueous solution by brine, as in the case of true or fatty acid soaps, and consequently is made separately. An excessive quantity of rosin in toilet soaps causes irritation of the skin, probably due to the hydrolytic dissociation of the alkaline salts of the weak abietic acids. In addition to its importance as a varnish, resin lac substitutes can be produced by dissolving casein in an alcoholic solution of rosin to give bright and transparent coatings. It is

By distillation under ordinary pressure abietic acid is decomposed into abietene and carbon dioxide.¹⁶ On distillation with small quantities of sulphur,



retene is produced (rosin spirit is rich in *m*-cymene¹⁷). Therefore abietic acid is decalhydrodimethylisopropyl-phenanthrene carboxylic acid. Pimaric acid has been stated to be the monomethyl derivative of abietic acid (Easterfield and Bagley), but Köhler¹⁸ gives to pimaric acid ($\alpha_n = -280^\circ$) the formula $(C_{20}H_{30}O_2)$. Rimnic acid (rimu resin) and podocarpic acids (podocarpus resin) are considered to be octo-hydro-oxy-methyl and octo-hydro-oxydimethyl-phenanthrene carboxylic acids respectively. P. Levy¹⁹ states that abietic acid contains a hexahydrogen benzene nucleus, an isopropyl group, and has its carboxyl acid group attached to a tertiary carbon atom. A. Grün²⁰ states that abietic does not contain two double bonds, for on treatment with concentrated sulphuric acid it gives an internal ester of an hydroxyacid, $(C_{19}H_{30}(OH)(CO-O-C_{19}H_{30}COOH)$. He considers abietic acid is built up like pinene and contains a bridge linkage and one double bond, on the assumption that molecules of α - and β -pinene ($C_{10}H_{16}$) unite with subsequent oxidation of a methyl grouping to a $COOH$ grouping. By different modes of combination of two molecules of pinene, a series of abietic and pimaric acids and other acids can be formed in an analogous manner from camphene or fenchene.

Tschirch²¹ considers that conifer resins fall into two groups; those containing abietic acid and those containing pimaric acid. The oleoresin from *Pinus palustris* (American oleoresin) contains abietic acid (acid value 188-192, and saponification value 237-257.6), whereas the oleoresin from *Pinus maritima* (French) contains *d*- and *l*-pimaric acids (acid value 171.5, saponification value 172-174). Canada balsam contains resins belonging to both groups. Abietic and pimaric acids are isomers possessing the formula $C_{20}H_{30}O_2$, differing in melting points and crystalline form, and abietic acid shows an apparent ester number, although esters are absent. Tschirch considers this as indicative of enol formation.

Dupont²² has shown that the rotation of *d*-pimaric acid is unchanged by the action of very dilute hydrochloric acid, but

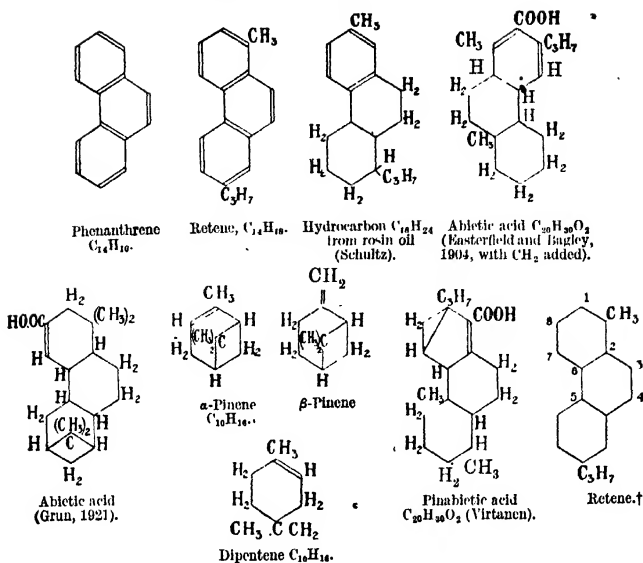
l-pimaric acid gives a decreasing rotatory power according to the length of time of contact with dilute hydrochloric acid. He considers that abietic acid in rosin is a mixture of isomorphous acids which he designates as pimarabietic acid, produced by the action of heat on the pimaric acids of the crude resin.

Aschan²³ has isolated from Swedish pine oil pinabietic acid, $C_{20}H_{30}O_2$, isomeric with abietic acid. It is almost insoluble in light petroleum, and possesses the remarkable property of being dextrorotatory in aromatic solvents and levorotatory in aliphatic solvents.

Stock²⁴ has investigated the distillation of rosin in high vacuum and found that the small difference between the temperature of boiling liquid rosin and that of its vapour indicated that rosin does not contain polymerised bodies of abnormally high molecular weight. He obtained crystalline acids from amorphous rosin by heating *in vacuo*, the time required to effect complete change depending on the temperature. He concluded that American rosin contains 31 per cent α -abietic acid, 31 per cent β -abietic acid, 19 per cent γ -abietic acid, 10 per cent resenes, 0.5 per cent essential oils, and 0.5 per cent impurities.

Recently O. Aschan²⁵ has separated from American and Finnish colophony a new series of rosin acids, colophenic acids: $C_{16}H_{22}O_4$, $C_{17}H_{24}O_4$, $C_{18}H_{26}O_4$, $C_{20}H_{30}O_4$, with melting points 96° - 105° C., 70° - 75° C., 80° - 90° C., and 80° - 90° - 100° C. respectively. They are amorphous monobasic acids, not decolorised by charcoal, and the yellow and brown colour of rosin, as well as the bitter taste, are said to be due to their presence. They are not insoluble in water, but are insoluble in petroleum ether. The alkali salts are soluble in cold water, distinguishing them from the salts of other resin acids. Aschan considers that the formula $C_{19}H_{28}O_2$ put forward by some investigators was due to the presence of these substances. They are unsaturated acids, and are probably oxidation products of abietic acid. By the action of hydrogen peroxide on sodium abietate, hexadecacolophenic acid, $C_{16}H_{22}O_4$, is produced, which reacts with phenylhydrazine and with acetic anhydride, indicating the presence of CO and OH groups. Fahrion²⁶ points out that these colophenic acids are probably identical with oxyabietic acids produced by the action of air on abietic acid; cf. oxidation products of linseed oil. The peroxide acids are unstable and undergo change to oxy- and ketoacids, which can react with acetic anhydride and phenylhydrazine.

A summary of the chemistry of rosin and rosin oil has been given by C. E. Soane (*Journ. O. and Col. Chem. Assocn.*, 1922, 5, 320). The following constitutional formulæ have been put forward for abietic acid and substances allied to it:



† According to Ruzicka, the remaining CH_3 group and the $COOH$ group in abietic acid may occupy one of the following positions: $-CH_3:COOH = 6:3, 5:4, 6:1, 2:8, 2:7$.

It would appear as if the formula $C_{20}H_{30}O_2$ were the most acceptable for abietic acid, and Easterfield and Bagley's type of formula is preferable to Grün's formula in the light of present knowledge. L. Paul²⁷ in a series of papers has investigated abietic acid very carefully, and finds that it has a number of modifications differing in melting point and solubility. American colophony is stated to contain 90 per cent γ -pinic acid (m.p. $75^\circ C.$); γ -pinic acid is obtained as a voluminous precipitate when a solution of rosin in alkali is treated with hydrochloric acid. Its melting point, $75^\circ-76^\circ C.$, rises in eight months to $88^\circ C.$ Sylvic acid (occurring in rosin) can be prepared from γ -pinic acid by the action of cold alcohol. The two acids are transformed on standing into α -pinic acid (m.p. $81^\circ-83^\circ C.$), which is soluble in water and in petroleum, and β -pinic acid (m.p. $98^\circ-100^\circ C.$).

α - and β -pinic acids are present in colophony, especially in colophony powder. When α - and β -pinic acids are crystallised from hot alcohol, α -, β -, and γ -abietic acids (m.p. $150^\circ C.$, $160^\circ C.$, and $162^\circ C.$ respectively) are obtained.²⁸ Cohn²⁹ prepares abietic acid from white rosin by recrystallisation on the water bath from methyl alcohol and ether (50:6) and washes the crystals of abietic acid (m.p. $156^\circ-162^\circ C.$) with methyl alcohol.

The formation of water-soluble pinic acids is worthy of con-

sideration as adding to the active acidity of films containing rosin and affecting their durability.

E. Knecht and E. Hibbert³⁰ obtained by repeated crystallisation from acetic acid and alcohol two pimaric acids ($C_{20}H_{30}O_2$) from American and French turpentine respectively, showing opposite optical rotations. On heating *in vacuo* or in a stream of carbon dioxide they are converted into rosin-like anhydrides, which on recrystallisation from acetic acid or alcohol change to inactive pimaric acids. The resins themselves probably consist of anhydrides, hydration being preliminary to the crystallisation of the resin acids, and it is suggested that this is the cause of whitening of the surface varnished with rosin when subjected to prolonged immersion in water.

The chief constituents of rosin must be considered as abietic acid in one or more of its many forms, colophenic, pinic, sylvic, pimaric, or sapinic, together with small quantities of resenes, which are soluble in neither acids nor alkalies, and are of relatively low oxygen content. The resenes may be regarded as oxypolyterpenes formed from terpenes by simultaneous polymerisation and oxidation. Abietic acid from Spanish colophony is identical with the acid obtained from American colophony.³¹ The modification of the abietic acid will depend on the variety of the oleoresin and on its age and mode of treatment to give colophony.

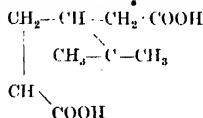
Klason and Köhler (*J. f. prakt. Chemie*, 1906, **73**, 337) found that the "winter resin" from Scandinavian pines yielded a mixture of sapinic acids, which are also the precursors of the type of resin acid in American colophony, whilst pimaric acids are characteristic of French galipot resin.

A pure abietic acid may be prepared by gently heating fifty parts of white colophony with a mixture of fifty parts of methyl alcohol and six to seven parts of strong sulphuric acid on the water bath, with frequent stirring and shaking until a crystalline mass is obtained; this is cooled, strained, and triturated with cold methyl alcohol. The resulting abietic acid melts at 156° - 162° C. and may be recrystallised from methyl alcohol. A sample of the pure acid heated at 160° - 170° C. gives, on cooling, a fused mass (s.g. 1.072), which shows no tendency to crystallise (white rosin has s.g. 1.08), and it behaves to ammonia, methyl alcohol, and strong sulphuric acid in the same way as ordinary rosin. By heating fused abietic acid to about 200° C. a yellow colophony (s.g. 1.07) is obtained. There is no loss of weight during the heating, and no anhydride is formed. These results indicate that rosin may be regarded as a more or less impure vitreous modification of abietic acid.

Unchanged γ -pinic acid (m.p. 75° - 76° C.) can be separated from rosin by treatment with very dilute ammonia and alcohol, because of the ease with which its ammonium salt is decomposed, whilst α -pinic acid can be obtained from the filtrate on acidification. γ -pinic acid gradually changes to α -pinic acid, which in turn changes to β -pinic acid (m.p. 100° C.). γ -pinic acid, sylvic acid, γ -abietic acid, are soluble in petroleum, whereas α - and β -pinic acids are insoluble.

L. Paul points out that rosin can form unstable compounds with organic and inorganic substances, as is shown in a very pronounced manner in its behaviour with petroleum hydrocarbons. Pure anhydrous γ -abietic acid is capable of absorbing benzene and higher boiling point hydrocarbons, and the same property is possessed by the salts of γ -pinic acid, especially the calcium salt. When sodium γ -pinate is heated with ten times its quantity of petroleum, water vapour is copiously evolved at 110° - 120° C. and the solution solidifies to a translucent mass. The application of this is shown in the function of thinners in resin varnishes, where the strong attraction of the resin for the thinner is a factor tending to the stability of the mixing. The work of Paul has been quoted at length, because it is an example of careful investigation into the properties of a typical resin in the behaviour of varnish mixings. The tendency to ignore these properties, except that of acidity, is likely to cause much trouble. β -pinic acid is characterised by solubility in water with the formation of fluorescent resin-like solutions. Sylvic acid is formed by the action of cold alcohol on colophony, whereas hot alcohol causes the formation of γ -abietic acid.

NOTE.— α - and β -pinic acids must not be confounded with pinic acid



produced by oxidation of α -pinene.

The colloid properties of colophony compounds and their changes are ascribed to a special holding power characteristic of resinous compounds with the formation of new chemical substances; e.g. γ -pinic acid forms weak compounds with essential oils which constitute the turpentine resins.

There is considerable difference of opinion in the views of investigators on L. Paul's conclusions. The crumbling of rosin on exposure to air is more probably an oxidation to give a peroxide acid,³² which is unstable and insoluble in petroleum ether, like many of the peroxide acids. It would seem as if β -pinic acid were an oxyabietic acid and not an isomer of γ -pinic acid. It is considered that anhydrides to the extent of 10-20 per cent are present with abietic acid in colophony, so that in the estimation of rosin in soap by alkalis the mean combining weight is taken as 346 and not as 302, which would correspond to $\text{C}_{20}\text{H}_{30}\text{O}_2$. The amount of unsaponifiable matter due to partial decomposition of the acid during distillation of the oleoresin varies with the source; e.g. French rosin gives 15.2, American W.W. 7.34, and American M. 7.61.

The following table will show the variations in acidity, saponification value, and iodine value of different varieties of rosin:

	A. V.	S. V.	I. V.
Austrian	146	167	116.8
American W.W. . .	154	183	92.3
" F. . . .	154	165	..
French	138	174	121.5-123

Reference has been made to the dispute as to the number of double bonds in rosin. A few figures given by Lewkowitsch will show that, in addition to absorption, considerable substitution occurs on treatment with bromine or iodine-carrying agents.

	Br. Absorption.	Added Br	Substituted Br.	I. V. (Wijs).	
W.G. Rosin .	210.7 ($\frac{1}{2}$ hr.)	41	85	219 (2 hrs.)	237.7 (24 hrs.)
W. Rosin .	203.5 (1 hr.) 201.8	88 114	58 43.0	159.9	195.8

These wide variations will be referred to later under Turpentine; $C_{20}H_{32}O_2$ (302) would require I.V. 168 for two double bonds. The function of rosin in a varnish mixing will be discussed in another chapter, but it is evident that the marked acidity of the substance, compared with the copals, will exercise profound influence on the properties of the mixings, and the presence of active double bonds will play a part in the oxidation process of drying. The decomposition of the resin oxidation products will have to be considered in respect to the durability of rosin varnish films.

Resinates.—Rosin yields, with alkalis, resinates or abietates (pinates), which resemble in many respects the alkali soaps made from oils and fats. The salts are easily hydrolysed by water and lather on being agitated. The rosin soaps may be salted out by addition of concentrated alkali or common salt, but not so readily or completely as in the case of soaps made from fatty acids. The sodium soap dissolves readily in alcohol, and the salts with alkaline earths and heavy metals are insoluble in water. The zinc, copper, and silver resinates are soluble in ether. The properties of the metallic resinates have been treated under metallic driers.³³

Fused resinates exhibit colloid characters in non-aqueous solvents and show variation in dispersion. Lead resinate solutions are stated to be more highly dispersed than those of cobalt and manganese (W. Schlick³⁴). Rosin films often show tackiness which can be corrected by addition of lime or zinc oxide, but the film is prone to hydrolysis by water. The powdery nature of the dried rosin film is characteristic, and is connected with the change of one pinic acid to another form, or with the transformation into an oxyabietic acid.

M. de Keghel³³ has described the use of resinates in lacquer paints and varnishes. When a dry precipitated resinate of zinc, aluminium, lead, or manganese is dissolved in turpentine and the solvent allowed to evaporate, a hard, vitreous, colourless varnish coating resistant to water is obtained, capable of replacing oil varnishes in numerous applications. If the powdered pigment be incorporated with this varnish, good quality lacquer paints are formed. The preparation of such paints is carried out as follows: The colour to serve as the pigment is carefully and thoroughly dried. The equally dry resinate is added, and the two ground and mixed together to give a fine homogeneous powder. The final mixing and grinding is carried out in a porcelain ball mill. The mass is then triturated with a little turpentine and is ready for use as a lacquer paint by simple dilution with a volatile solvent. When heavy pigments, such as lead, barium, and mercury compounds are used, it is advisable to make the turpentine paste thick, to avoid settling out of the pigment on storing or transport. The mixture of pigment and resinate cannot be made in all proportions, and preliminary experiments are always necessary to determine those proportions suitable for obtaining a coating which will be at once opaque and pliable and will have no tendency to rub off or to crack. The last mentioned is the most frequent trouble with this class of paint, and is often attributed to an excess of resinate. The addition of a little rosin oil to the paint does much to counteract the tendency to crack, and 4.5 per cent of rectified pale rosin oil should be added to the turpentine when the danger of paint-coat cracking is present.)

Two typical formulæ may be given here. For a white lacquer paint: zinc oxide, 20 parts; zinc resinate, 10 parts; neutral rectified rosin oil, 1.5 parts; turpentine, 25 parts. For a green lacquer paint: ultramarine, 20 parts; chrome yellow, 16 parts; aluminium resinate, 12 parts; manganese resinate, 2.5 parts; neutral pale rosin oil, 2.6 parts; turpentine, 52 parts. The rosin oil is dissolved in the turpentine, mixed with a finely ground pigment and resinate mixture, and the whole then pounded in cylinders. The resultant paint is immediately transferred to receptacles with tight-fitting lids.)

The lacquer paints are stated to be far more brilliant than the ordinary oil pigment paints. Their fastness and permanence may be greatly augmented by covering them with a pure transparent colourless resinate varnish; e.g. a 6 per cent solution of zinc resinate in turpentine to which 2 per cent of rosin oil has been added. The two layers being of the same chemical composition, an intimate union with perfect adherence is formed, and there is no danger of the protecting layer cracking or splitting off. In the opinion of the writer, although the brilliancy of the lacquer paints may be greater than that of the ordinary oil paint, it is doubtful whether they are sufficiently durable on exposure to atmospheric action.

Production and Consumption of Rosin.—The production and

consumption of rosin will be generally considered under Turpentine. The following table is taken from German sources : ³⁵

	Rosin.	Turpentine.	
	Tons.	Tons.	
U.S.A.—			
1913-14 .	350,000	150,000	
1914-15 .	420,000	11,000	
1918-19 .	245,000	63,000	
1920-21 .	321,000	88,000	
France—			
before 1914	64 to 80,000	19 to 25,000	10,700 tons of rosin and turps exported to England 11,900 do. exported to Belgium 6,600 do. exported to Holland In 1913, 43,000 tons of rosin and turps were sent to England
1919 .	110,000	35,000	
Spain, 1920-21 .	21,000	6,000	
Portugal—			
1919-20 .	6,300	1,800	
1920-21 .	12,400	3,600	
Greece—			
before 1914 .	9,400	2,300	

France is increasing her production of rosin and turpentine, whilst in America the supply is on the down-grade ; further, the cost of production there has risen, owing largely to the increased cost of labour.

The importation of rosin into the United Kingdom is as follows (in tons) :

	1919	1920.	1921.
From			
U.S.A.	57,240	31,283	19,401
France	21,366	22,568	14,155
Spain	9,617	4,860	6,151
Other countries .	798	1,765	1,237
	89,021	60,476	40,944

Rosin Esters.—In view of the serious defects of rosin referred to in the previous chapter, attempts have been made to replace it by rosin esters. (Rosin esters can be obtained by condensation of rosin with alcohols ; *e.g.* glycerol, resorcinol, and naphthol. Such esters are not soluble in caustic alkalies, in contradistinction to the behaviour of other resins. They are partly soft, partly hard, resin-like bodies which are suitable for varnishes. The esters of the sweated copals can also be used, but their solubilities in vegetable oils are less than those of the parent sweated copals.)

(The method of preparation is to heat the resin with the alcohol under pressure, with or without a dehydrating agent (acids or acid

alts). As an example may be given the preparation of the resorcin ester of rosin, by heating rosin, sweated *in vacuo* to 350° C. to remove volatile products, with 17 per cent of its weight of resorcin to 280° C. in an autoclave under several atmospheres pressure. The liberated water is allowed to escape and the heating continued until the ester formation is complete, which is determined by testing an ether or benzine solution of the ester with soda. When the esterification is complete, the solution will be unacted on by the soda. Dehydrating agents, such as hydrochloric acid, sulphuric acid, 1-2 per cent boric acid, or glacial acetic acid, may be used. Such esters can be incorporated with linseed oil at 300° C. By addition of a small percentage of lead oxide and baryta, and by passing in a stream of carbon dioxide or an indifferent gas, a clear pale varnish may be obtained. The general method for the glyceryl rosin esters is to heat rosin (600 lb.) in a copper still to 180°-200° C., and to the melted mass 10-25 per cent (72 lb.) of its weight of glycerine is run in and the temperature raised eventually to 280° C. for twenty minutes, until the acid value is reduced to 5 or 10; 3 lb. of quicklime are then incorporated to complete neutrality. Heating may be done *in vacuo* at 10 mm. to remove the water formed in the reaction, or by using a still-head the water with the excess of glycerine may be distilled off. The end of the reaction can be determined by treatment of the ethereal solution with soda, which ought to give no water-soluble extract. If the hardness is to be increased, it is advisable during the last stages of heating to add linseed oil, whereby the mass acquires a stouter consistency. Lead or manganese oxides may be added at the end of the process, so as to provide the necessary driers.)

The reduction in the acidity varies with the conditions of manufacture (temperature, time of heating, and amount of glycerine). The acidity of the original rosin may be reduced from 134 (sweated rosin) to 3. A hard ester-gum can be obtained by melting rosin with 10 per cent Congo copal, cooling to 550° F., adding 12 per cent glycerine, and heating to 555° F.³⁶ If an aluminium vessel be used instead of a copper the percentage of Congo copal, which can be esterified with rosin, can be raised from 10 per cent to 75 per cent. It would appear as if copper acted as a polymerising catalyst, causing the mixture to set and preventing the formation of glycerides. The esters are slightly soluble in alcohol, soluble in turpentine, linseed oil, ether, and petrol.

{ The advantages of the esters are good colour and chemical neutrality. They yield varnish mixings which can be made up with acid colours without causing "livering," and moreover their resistance to the action of weathering agents makes them superior as regards lustre to copal or rosin varnishes.*' In Circular 101, *Paint Manufacturers' Association, U.S.A.*, 1920, is described the manufacture of a substantially neutral glycerine rosin ester, with the aid of tung oil as esterifying catalyst, named "Tunga-resin."

* After a couple of years' exposure the films show fine cracks typical of rosin varnishes.

In the same communication there is a summary of the patents relating to the preparation of ester gums.

According to Gardner, limed rosin does not combine freely with glycerol, but his statement that rosin and glycerine alone do not combine freely is not in keeping with the experience of other workers, nor that glycerine combines more readily with rosin in the presence of tung oil if lime be added in the form of a soap of that oil. It is difficult to agree with the view that lime tungates formed stimulate the ester formation or act as catalysts. H. Wolff³⁷ recommends neutralisation of one-tenth of the acidity of the rosin by lime, with the addition of the calculated quantity of glycerine for the remaining acidity, and heating *in vacuo* to 300° C. If the product be too soft, part of the ester can be driven off by distillation.

Gardner³³ gives a table showing the variation in solubility of the esters with the acid values :

Rosin Ester.	Acid Value.	Colour.	Solubility in Alcohol.
No. 1	158.9	Very pale	Soluble in cold alcohol
No. 2	119.6	Light colour, opaque	but "cloudy" partial solution
No. 3	27.4	Medium, opaque	Dark in colour
No. 4	22.3	Medium, pale	Unaffected by alcohol
No. 5	17.2		
No. 6	8.18	Very pale, slightly cloudy	Softened, but not "dissolved"
No. 7	16	Dark brown, very hard	Unaffected

The properties of ester gums have been investigated by Ellis and Rabinovitz,³⁸ with special consideration for preventing livering of the vehicle in the presence of pigments. This paper is of interest in giving a summary of the published work to date. Rosicki³⁹ considers that the reduction in acidity of the resins is a necessary condition, whereas Muehle⁴⁰ is of opinion that the coagulation (livering) is due to association of copal particles rather than to the formation of insoluble salts, because he was unable to produce varnishes from Congo and Manila copals which would stand the addition of pigments after previous esterification or reduction in the acid value. Meguelo⁴¹ considers there is truth in both views, and the verdict of practical experience will support him.

It must be pointed out that varnishes containing rosin glycerides will not show the rosin coloration in the Liebermann-Storch reaction (*q.v.*). Instead of a fugitive purple coloration a fugitive rose-red colour is obtained.

Rosin Oil.—When rosin is submitted to the action of heat, as is done on a large scale in stills holding many tons, the products consist of water, combustible gases, and a series of oils of increasing gravity and viscosity as the distillation proceeds. The heating

may be by direct fire or by superheated steam. The conditions of distillation modify the proportions of the products. The products consist of—

	Dry Distillation.	Fire Heat and Superheated Steam.
Gas, per cent . . .	5.4	..
Acid water, per cent .	2.5 (containing 10 per cent acetic acid)	..
Rosin spirit, per cent .	3.1	15.0
Rosin oil, per cent .	85.1	64.0
Pitch, per cent . . .	3.9	..

The rapidity of the distillation has an effect on the proportion of the products. Hard rosin oil (s.g. 0.9946-0.9982, 18-31 per cent rosin acids) is produced when the distillation is conducted rapidly and during the first stages of distillation, whilst soft rosin oil (s.g. 0.9878, 9.2 per cent rosin acids) is produced when the process is conducted slowly, and especially during the middle period of the distillation (Lewkowitsch). The light oil which comes over below 200° C. is termed rosin spirit. The heavier oils, which vary from pale yellow to deep brown, constitute rosin oil and form the greater bulk of the distillate. They usually show a blue or green fluorescence. The gas is of value for illuminating purposes, and from the acid water calcium acetate is prepared. The properties of rosin pitch will be referred to under Pitches. In France the addition of lime to the rosin causes an alteration in the composition of the products. For the paint and varnish industry the demand for rosin oil is insignificant compared with its use as a lubricant. A summary of the manufacture of rosin oils and their uses has been given by McG. Shuey.⁴² The direct distillation of American rosin (B grade) by superheated steam or by direct fire gives (1) water; (2) rosin spirit, s.g. 0.93-0.94, straw coloured, 1 per cent yield; (3) thin oil, s.g. 0.98, 6 per cent yield; (4) first run oil (kidney), s.g. 1.003-1.01, containing 44 per cent of abietic acid (kidney oil distils over at 200° C. and always shows a brownish shade on standing, and the yield is 70 per cent); (5) bloom oil distils over at 360° C. and its colour is amber to almost black, with a yield of 6 per cent and containing 14-16 per cent of rosin acid. As soon as the bloom oil begins to distil, the heating is stopped, otherwise the rosin pitch would begin to coke.

The rosin oil is purified by removal of the rosin acids by alkalis. Renard⁴³ isolated from rosin oil a hydrocarbon, diterebenthyle, $C_{20}H_{30}$ (b.p. 343°-346° C.). Krämer and Spilker⁴⁴ by distillation of rosin oil under pressure isolated cymene, methyl cymene, phenanthrene ($C_{14}H_{10}$), and methyl phenanthrene. Virtanen⁴⁵ prepared a series of hydrogenised retenes, and after comparing them with the hydrocarbons of rosin oil, concluded that all rosin acids contain a hydrogenised retene nucleus. There is now practical

unanimity upon that conclusion, but there is still disagreement as to the position of the side groups. In the meantime the differences in the relative positions of the methyl and isopropyl groups may account for the isomerism in the resin acids.⁴⁶ Rosin oil consists essentially of a mixture of hydrocarbons of the hydrogenised retene type, together with those decomposition products of a benzenoid character, which would result from a cracking process as the higher temperatures of distillation are reached.

Rosin oil has the greatest power for penetrating paper of any known oil, a property to which it owes largely its extensive use in the manufacture of printing ink and of electric cables. It is a poor conductor of heat and electricity.

Paper-wrapped electric cables are soaked in rosin oil, because of its high penetrating power and low electric conductivity.

The better qualities of rosin oil have no drying properties and the crude varieties are generally feeble in that respect, although Shuey (*loc. cit.*) states that the capacity of rosin oil for absorbing oxygen gives rise to drying qualities which make it useful in varnishes; a statement which must be qualified.

Rosin oil differs from mineral oil in a number of characteristic properties, so that its estimation in mixtures of the two substances rests on its higher specific gravity, greater solubility in alcohol, acetone, and glacial acetic, and higher refractive index. The estimation of rosin oil depends generally on its acidity, due to the resin acids which distil over with the oil (C. E. Soane, *loc. cit.* p. 138).

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CHAPTER IX

JAPAN LAC AND SYNTHETIC RESINS

Japan Lac and Burma Black Varnish.—*Japan Lac.*—There are two genera of plants, belonging to the natural order Anacardiaceæ, containing species which on being tapped yield a sap largely used in the East as a natural varnish or lacquer; these are *Rhus*, which yields Japanese lacquer, and *Melanorrhœa*, which furnishes the black varnish of Burma.

The Japan or Chinese lacquer is characterised by (1) hardness, which increases with age; (2) lustre, which is retained under varying atmospheric influences; and (3) resistance to the usual agencies which attack varnishes.¹

The tree which yields Japanese and Chinese lacquer is *Rhus vernicifera* (Tsi-chou, varnish tree). It is found in woods at an elevation of 4000 ft. and cultivated along the margins of fields or in valley bottoms. The tree reaches a height of about 10 metres with a diameter of 0.40 m. The tapping of the tree resembles that of *Pinus* for turpentine oleoresin. In China the collection is made in June or early July; gashes are made in the trunk and the juice is collected in shell-shaped iron plates. The plates are cleaned out by the moistened finger into a bamboo pail carried by the collector. The contents of the pail are placed in a barrel and covered with hemp paper. Each tree is tapped seven times in one year at intervals of seven days, and left for five to seven years to recover.* The vapours disengaged from the lac are said to produce very painful boils, which, however, do not cause death. Large quantities of the varnish pass annually through the port of Hankow. In 1908, 2,479,702 lb. were exported, the bulk of which went to Japan. There are three kinds of Japan lac, viz. Ro-iro (best), Hana (medium), Se-shi (inferior). The raw varnish, which is frequently adulterated with tung and perilla oils, is known in Japan as Ki-urushi.

When freshly collected the sap is of a grey-brown colour and a viscid consistency, turning reddish black on exposure to the air and becoming coated with a thick tough skin. All the varieties

* An acre will support a thousand or twelve hundred trees and may produce from four to ten gallons of varnish in ten years (Sabin). A large tree is estimated to produce 90 grammes, while a small tree produces only 56 grammes of the gum (*Journ. Soc. Chem. Ind.*, 1910, 29, 1320).

of varnish contain water, which is made to disappear by stoving or on exposure to the sun.

To imitate the black varnishes of Japan, the Chinese add oil of tea boiled with grey and red arsenic and incorporated with bone black. Sabin (*loc. cit.*) gives a translation of a memoir by D'Incarville (1735) on the mode of collection and application of the lac, which is an important addition to the knowledge on the subject. The French Jesuit missionary claimed no knowledge of varnish in general, and simply records his observations of a process which had been kept secret for centuries. A more detailed account is given by J., J. Quinn,² and a concise account of the Chinese and Japanese lacquer manufacture will be found in the *Bulletin of the Imperial Institute*,¹ and in Stewart Dick's *Arts and Crafts of Old Japan*.³ The only method of thinning the lacquer is said to be by the addition of camphor, but it is easily soluble in cyclohexanol. The peculiarity of the varnish is that it hardens only in a moist atmosphere, and remains in a tacky condition if exposed to sunlight and heat. In Peking, where the air is very dry, it is necessary to expose the lacquered work in a humid place surrounded with matting which is kept damp, otherwise the varnish will not dry; or the varnished articles must be surrounded by soft damp linen (Coffignier). The proceedings in Japan are similar to those in China, from which they are originally derived. Oxygen to 5.75 per cent by weight is absorbed in the drying at the ordinary temperature. Whether the catalyst is a ferment (laccase), or whether the activity is due to the presence of manganese with a proteid substance, is undecided. It is stated that if the lac acid be extracted with alcohol it will not dry in the absence of a nitrogenous enzyme. If the lac be heated above 60° C. the drying of the lacquer is inhibited. It is also stated that the proteid acts as a ferment upon the lac acid, causing the latter to become oxidised and hard. The oxidised lac acid is insoluble in all the solvents of the original lac and is unacted on by acids, except by hot concentrated nitric acid, and alkalies. The ordinary oil driers hasten the setting and hardening, which are retarded by acids, alkalies, and certain metallic salts. The lac dries better in winter than in summer: nevertheless, it can be stoved at 100° C., or more rapidly at 150°-180° C., with the formation of a hard, durable, resisting film. It darkens at high temperatures, so that for clear lacquers the temperature must not exceed 120° C., and for dark lacquers, 180° C. :

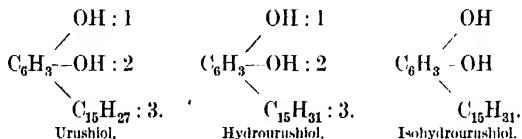
(The application of the lacquer is said to be dangerous to western workers owing to the peculiar poisonous properties of the urushiol in the resin, but recent experience has shown that these have been much exaggerated. No doubt further investigations will render the lac more popular on account of its great weather-resisting properties. For aeroplane propellers it is the best coating for durability as yet known. It is stated that turpentine can be used to thin the varnish and, if the film is not too thick, it will dry under ordinary conditions, but moisture facilitates the hardening.

(The resin has been thoroughly examined by Japanese chemists,

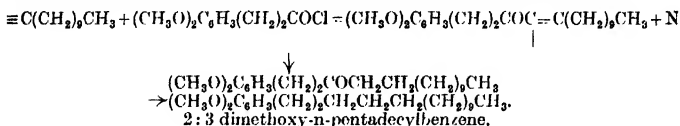
especially Yoshida and Majima, the latter having effected a synthesis of hydrourushiol dimethyl ester obtained from urushiol, the chief constituent of Japan lac.

Lac of the first quality has the following composition : Urushic acid, 85.15 ; gum arabic, 3.15 ; nitrogenous material, 3.28 ; water and volatile matter, 9.42.

Urushic acid is soluble in alcohol, ether, chloroform, etc. Tschirch and Stevens⁴ showed that the urushic acid of Yoshida is a phenolic substance. The yield of this acid is 60-80 per cent, depending on the locality. Urushic acid is now called urushiol, which is the active principle of Japan lac. On reduction by hydrogen and platinum, urushiol ($C_{21}H_{33}O_2$) gives hydrourushiol ($C_{21}H_{36}O_2$), and it also yields (on heating to 350° C.) pyrocatechin. On oxidation by potassium permanganate it gives oxalic and palmitic acids.



Majima and Tahara⁵ consider urushiol, containing 10 per cent of hydrourushiol, to be the principal constituent of lac and have synthesised hydrourushiol dimethyl ester from sodium dodecine and 2 : 3 dimethoxyphenylpropionyl chloride, with subsequent reduction :



3 : 4 dihydroxy-*l*-pentadecylbenzene was also synthesised and found to be identical with isohydrourushiol, which had been obtained by Majima and Nakamura by heating pentadecanic acid with pyrocatechin and reducing the ketone formed, whereby isohydrourushiol (m.p. 91° C.) was produced.

Urushiol is a mixture of compounds which differ from one another in the number and in the position of the double bonds present in the long normal carbon chain. In this respect it exhibits a close similarity to drying oils. These components are converted into the same hydrourushiol. One compound, $C_6H_3(OH)_2(CH_2)_7CH : CH(CH_2)_6CH_3$, gives on oxidation an acid, $C_6H_3(OH)_2(CH_2)_7COOH$, and heptanal, whilst another, $C_6H_3(OH)_2(CH_2)_7CH : CH(CH_2)_4CH : CH_2$, gives formic acid and the same acid as from the preceding compound.*

Burma Black Varnish.—The Burma black varnish (thitsi) is an oleoresin obtained from the black varnish tree, *Melanorrhœa usitata*. The trees are tapped and the properties of the oleoresin

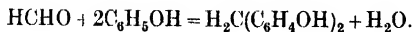
* The main constituent of Indo-Chinese lac (laccol) has the constitution $C_6H_3(OH)_2(CH_2)_5CH : CH(CH_2)_6CH_3$ (1 : 2 : 3).⁶

are similar to those of the lac obtained from rhus, although slower in drying.⁶ Thitsi contains thitsiol, $C_6H_3(OH)_2C_{17}H_{35}$ (1 : 2 : 4), which is an unsaturated substance, reducible to hydrothitsiol (4-n-heptadecylcatechol).⁵ It is not present in thitsi in such large amount as is urushiol in Japan or Indo-China lac.⁷

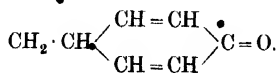
SYNTHETIC RESINS

Phenol-formaldehyde Resins.—When phenols and formaldehyde (formalin) are heated in the presence of condensing agents, substances are obtained which in appearance and in properties resemble varnish resins. The condensing agent may be an acid, an alkali, or ammonia. The investigation of these substances has been developed by Bakeland⁸ and his collaborators. The chief representative of this class is Bakelite, which is manufactured in a number of forms, each with important properties.

Bakelite.—An account of Bakelite and its applications is given by Lebach.⁸ The so-called Bakelite varnishes are solutions of Bakelite A in methylated spirit. The varnishes when stoved give hard insoluble and infusible coatings of high chemical and mechanical resistance. Stoved Bakelite lacquer films resist the action of methylated spirit, ammonia, and salt water; moreover, they are acid-proof. If fluid Bakelite A (resol) is heated for several hours at a temperature of 140°-170° C. and under a pressure of 10 atmospheres, it is transformed into transparent insoluble and infusible resite. Generally a filling material is used which is impregnated with the fused resol, forming a plastic mixture, and completely fills the mould in the press. At a temperature of 100°-200° C. the resol is changed to Bakelite C (resite). Resite is non-hygroscopic, and is one of the most resistant of all plastics. It can be heated to 300° C. without decomposition, and at higher temperatures it chars, but does not ignite. It is an excellent di-electric, and is suitable for pen and pencil holders, umbrella handles, cigar holders, etc. The action of an aldehyde on a phenol is primarily according to the scheme



Wohl⁹ considers the resites to be polymerisation products of the methylene derivatives of a tautomeric phenol.

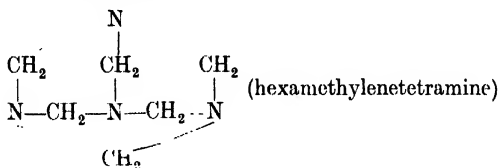


Herzog and Kreidel¹⁰ attribute the capacity to polymerise to the presence of the resinophone group $CH : CH : CO$.

Coster van Voorhout¹⁰ has supplied more definite information as to the course of reaction between phenol and formaldehyde. He followed up the viscosity changes occurring during the con-

densation, and has isolated products from the reaction mixture. He was able to separate crystalline ortho- and para-oxybenzyl alcohol when an alkaline catalyst was used, and detected the presence of dioxydiphenylmethane when the condensation was initiated by acids. His conclusions as to the composition of Bakelite are that it consists most probably of a mixture of dioxydiphenylmethane, probably polymerised, with traces of phenol and formaldehyde, in accordance with the simple reaction shown above. Progress in the manufacture of phenolic condensation products has been principally in the direction of knowledge of the conditions of reaction to the attainment of specific properties in the final product. Thus, solubility to the point of obtaining alcohol- and oil-soluble resins is claimed to be obtained by restriction of the reacting phenol to *o*-cresol; *m*-cresol is said to be more suitable for the preparation of spirit-soluble resins, and moreover it reacts more easily with formaldehyde. For oil-soluble products *p*-cresol is recommended.

To effect the condensation three classes of catalysts are employed: acids, ammonia, and caustic alkalis, and consideration must be taken of the proportions of phenol and formaldehyde used. If ammonia be used with formaldehyde, hexamethylenetetramine is first formed, which reacts with phenol in the proportion of 3 mols. phenol to 1 mol. hexamethylenetetramine ($(\text{CH}_2)_6\text{N}_4$), to produce a well-defined crystalline product $(\text{C}_6\text{H}_5\text{N}_4\cdot 3\text{C}_6\text{H}_5\text{OH})$.¹¹ Under the action of heat this product undergoes decomposition, probably according to Voorhout's scheme, and resinifies with the evolution of ammonia.⁸ *m*-cresol yields a diphenol substance, $\text{C}_6\text{H}_5\text{N}_4\cdot 2\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$; *o*-cresol yields a monophenol. Resorcinol reacts similarly.



Harvey and Baekeland¹² do not consider that this formula is properly represented to account for the above compounds. Instead of ammonia, the ammonium salt of a volatile acid or amine (fatty or aromatic) may be used. Instead of an alkali or alkaline, carbonate sodium sulphate can be employed. W. Esch¹³ condenses phenols or *o*- and *m*-cresols or their derivatives with an aqueous solution of an aldehyde in the presence of benzoates or salicylates as catalysts. Satow and Sekine¹⁴ state that the solubility, fusibility, and the chemical and physical resistance of the condensation products are proportional to the degree of condensation, and that the oil-soluble condensation products from phenol and formaldehyde give distinctive colour reactions with many salts, whereby it was found that the nature of the condensation product varies with the catalyst (acid, ammonia, and caustic alkali). The patents for the preparation of these resins are very numerous, and a summary of them appears

in the Annual Reports of the Society of Chemical Industry. Ragg¹⁵ considers that their high price will prevent their employment on a large scale, but for special uses the superior properties will permit of their application. He classifies the formaldehyde resins into four classes:

(1) Insoluble in the usual solvents and infusible (Bakelite and resites).

(2) Soluble in certain solvents, but giving a lacquer which must be stoved to give a durable coating (Bakelite A and B).

(3) Resinites soluble in alcohol and giving usable varnishes without stoving; *e.g.* Issolin.

(4) Resins soluble in fatty oils and other solvents—Albertols (Albert and Behrend).¹⁶

Class No. 4 is of especial interest, and the use is only restricted by the high cost compared with that of the natural oil-soluble resins.

As a lacquer substitute the Bakelite A type has become popular, and gives a coating of high lustre and good colour. Colourless transparent synthetic lacquers have not as yet been obtained of the same durability and lustre as the gold stoving varieties.

H. Wolff¹⁷ points out that with solvents employed in solutions of synthetic resins the increased viscosity arising on addition of non-solvents induces a change from molecular to colloidal solution, and even to gel formation. He suggests that the persistent softness of residual films resulting from exposure of resin solutions is to be accounted for by the selective evaporation of the true solvent. This would not occur in varnishes containing turpentine, because the slightly less volatile turps is the best solvent; but in a blend of xylol and petroleum the concentration of the less volatile solvent would increase on drying and favour gel formation and softness of the film. This will be referred to under Turpentine Substitutes, and is a point which is very often overlooked. Beckmann and Dehn¹⁸ describe a series of resins, similar to Bakelite, in which furfural aldehyde takes the place of formaldehyde or benzaldehyde.¹⁹

Cumarone Resins.—A new class of artificial resins, the cumarone resins, has attracted attention lately. They are polymerisation products of cumarone and indene, obtained from coal-tar naphtha distilling between 160° and 185° C., by the action of sulphuric acid.²⁰ The details of the preparation of cumarone and indene resins by polymerisation are given by Barrett.²¹ Marcusson²² notes the greater solubility of cumarone resins in solvents, and generally the lower melting point, temperature, and lower acid, saponification, and iodine values than the natural resins.

The polymerisation may be effected by aluminium chloride at 20° C.; the lower the temperature of polymerisation, the higher the melting point and the lighter the colour of the polymerisation products.

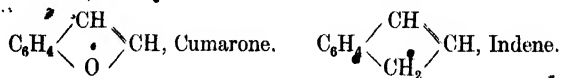
E. Stern²³ found that zinc chloride and silicon tetrachloride did not induce polymerisation, but that stannic chloride had a pronounced effect. The action of aluminium chloride was not due

to the liberation of hydrochloric acid. The cumarone resin is easily soluble in benzole and its homologues, but is insoluble in methylated spirit. The films are surprisingly water-resisting, but they have not the fine lustre of the Bakelite resins on stoving. They are, however, superior to them in resisting atmospheric influences, and in that respect are much better than shellac coatings. At present their high price restricts the use of the resin except for special purposes. Lately there has been improvement in their manufacture, as the earlier varnishes gave tacky films and, although hardened by the addition of para-indene, their durability was poor.

E. Glaser²⁴ states that cumarone resin is produced from the residues remaining from the careful distillation of light benzole, heavy benzole, and carbolic oil (tar oil fractions, b.p. 160°-200° C.), after these have been freed from pyridine bases and phenols by washing with a carefully regulated quantity of concentrated sulphuric acid, avoiding excess. It is essential to obtain a thoroughly intimate admixture of the acid and the oil. For this purpose mechanical agitation has largely displaced air agitation, on account of the high benzole losses. The acid is added in small quantities at a time, as this has been found to give better results than by adding all the acid in one charge; generally 5 per cent by weight of sulphuric acid is added. Superheating during distillation should be avoided. The shrinkage in volume due to the absorption of unsaturated compounds by sulphuric acid may amount to 12 per cent in inferior oils, and is generally about 8 per cent. Two parts solid resin are furnished by 1000 parts of tar.

Indene (Kraemer and Spilker, 1890) is found in the crude benzole fraction (b.p. 176°-182° C.).

Sulphuric acid converts cumarone into para-cumarone and indene into para-indene, three polymerides being known. With concentrated sulphuric acid a polymeride (m.p. 210° C.) is obtained which dissolves in ether with difficulty. With weak sulphuric acid a polymeride (m.p. 100° C.) is obtained which is easily soluble in ether. It is the presence of this modification which is the cause of the low melting point of many cumarone resins. Cumarone is a colourless liquid (b.p. 172° C., s.g. 1.096) and is polymerisable. Para-cumarone (m.p. 107°-108° C., m.w. 473, $(C_8H_6O)_4$) has two modifications, one soluble and the other insoluble in benzole.



From its formula it is suggestive of the resenes referred to under the copals; moreover, the inactivity of cumarone is worthy of more consideration.

R. Fischer²⁵ compares the prices in Germany of cumarone resins with American and French rosin:

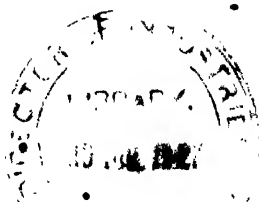
- 100 kilos cumarone resin cost 250 marks.
- 100 kilos American rosin cost 385-450 marks.
- 100 kilos French rosin cost 320-490 marks.

The production of cumarone resin in Germany in 1917 amounted to 11,000 tons.^{25a}

Duroprene ($C_{10}H_{13}(Cl)_m$).²⁶—By the chlorination of rubber a solid resin is obtained, soluble in benzol, coal-tar naphtha, carbon tetrachloride, and trichlorethylene. The ordinary Duroprene varnish is a 10 per cent solution of the resin in benzol and solvent naphtha. The varnish film is unacted on by alkalis and acids, alcohol, ether, petrol, and paraffin oils. The advantages claimed for it by the United Alkali Co. demand careful consideration in view of its valuable protecting properties, impermeability to water, and the pale colour of the varnish film. It would seem to be superior to many spirit varnishes, but the film of the resin lacks the elasticity given by an oil varnish.

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CHAPTER X

BITUMINOUS SUBSTANCES

Varieties of Bituminous Substances.—It is difficult to give strict definitions of the various bituminous substances used in industry. The terms “bitumen,” “asphalt,” “tar,” “pitch,” “resin,” and “wax” overlap in their meaning, which thus becomes indefinite.

The term bitumen is considered by Langton¹ to be generic, denoting a class of substances soluble in carbon disulphide and other neutral liquids, and consisting of compounds of carbon and hydrogen, associated frequently with compounds of oxygen, sulphur, and nitrogen. Asphalt is regarded as mineral matter containing bitumen in intimate association. Bitumens may be classed according to origin, natural or mineral, artificial or pyrogenous. The mineral pitches comprise bitumen (Sanskrit-Latin equivalent *gwitūmen*, pertaining to pitch) or asphaltum (*ἀσφαλτις*, stable; French *asphalte*; Spanish *asfalto*; German *Erdpech*). The pyrogenous pitches are produced by the distillation or destructive distillation of carbonaceous material, either in closed vessels or by blowing in air during the distillation. They appear in the form of petroleum pitch (the residual pitches produced in the distillation of asphaltic and non-asphaltic petroleums), coal-tar pitch, resin pitch (from the destructive distillation of resinous woods and resin, e.g. Stockholm pitch and rosin pitch), stearine pitch (from vegetable and marine oils), wool grease pitch (from wool fat), and bone pitch (from the destructive distillation of bone-oil).

Colour, consistency, hardness, lustre, fracture, volatility, odour, feel, and fusibility, as well as solubility in special solvents, are their most important physical characteristics, distinguishing the members of the different classes of pitches or bituminous substances. The differences in chemical composition, though varied, are not of such decided importance from an industrial standpoint as the physical properties mentioned above.

In the table on following page the generic term bitumen includes petroleum pitches, native asphalts, native mineral waxes, and asphaltites. Asphalt includes native and pyrogenous asphalts. Native asphalts are often associated with a substantial proportion of mineral matter. Pyrogenous asphalts include the residues obtained from the distillation, with or without air-blowing, of petroleums. The asphaltites include gilsonite or glance pitch and grahamite, whilst the pyro-

	Origin.	Colour in Mass.	Consistency.	Lustre.	Feel.	Volatility.	Fusibility.	Solubility in CS ₂ .	Sulphonation Residue of 300°-350° C. Distillate.
Bitumen (generic term)	Native	Variable	Variable fluid to solid	Variable	Harder varieties fusible	Largely soluble	Considerable
Pyrobitumen (generic)	"	Dark	Comparatively hard	Resinous to dull	Non-adherent	Non-volatile	Infusible	Relatively insoluble	"
Asphalt	Native or pyrogenous	"	Variable	Harder varieties resinous to dull	Adherent to non-adherent	Comparatively non-volatile	Fusible	"	"
Asphaltes and Asphaltic Pyrobitumens	Native	"	Comparatively hard	Resinous	Non-adherent	Non-volatile	Difficulty fusible or non-fusible	" Asphaltites largely insoluble	"
Pitch (generic)	Pyrogenous	"	Viscous to solid	Resinous to dull	Adherent to non-adherent	Comparatively non-volatile	Fusible	Soluble	"

bituminous asphaltites include impsonite and elaterite. Pitch comprises the residues from the distillation of tars (oil-gas-tar pitch, water-gas-tar pitch, bone-tar pitch, wood-tar pitch, coal-tar pitch, producer-gas-coal-tar pitch, and other coal-tar pitches, as well as pitches produced on distillation of fusible organic substances), the process having been terminated before the formation of coke, *e.g.* rosin pitch and stearine pitch. Only those pitches which are used in the varnish industry will be treated in detail, so that the description of the classes of bituminous substances will be very restricted.

Before 1902 the term asphalt was confined almost exclusively to certain semi-solid or solid bitumens found in natural deposits, most of which occurred in admixture with clay or sand, which could not be removed by ordinary refining methods. When the mineral matter predominated the product was termed asphaltic sand or rock asphalt, depending upon whether or not the mineral structure was loosely or firmly knit together. The European rock asphalts contain less than 15 per cent of bitumen, whereas refined Trinidad asphalt (Manjak) has 56.5 per cent, so that until 1892 Trinidad asphalt was so generally used that the term asphalt was applied to that coming from Trinidad. In 1892 a relatively pure asphalt occurring in Venezuela (Bermudez Lake Asphalt) was brought into the market, and the import into the United States is now nearly equal in tonnage to that of the Trinidad asphalt. Comparatively small deposits of asphaltic sand and rock asphalt have been found in the United States, *e.g.* gilsonite (Utah), grahamite (Oklahoma), and wurtzelite, and have been used for asphaltic specialties, of which black japans are the most important; but (as will be seen later) the demand is small compared with the requirements of the two main asphalt industries, paving and roofing.

Before describing bitumens and pitches in detail, it is advisable to indicate briefly the chemical composition of the former class, with the object of tracing connection between chemical composition and physical properties. The bitumens are essentially hydrocarbons containing small and variable amounts of oxygen, sulphur, and nitrogen, but the hydrocarbon character is the dominant feature. The hydrocarbons may be paraffins of the C_nH_{2n+2} series, the gaseous members of which accompany the liquid forms in Pennsylvania petroleum, and the solid members ($C_{24}H_{50}$ and upwards) are found in ozokerite and paraffin wax.

The members of the olefine series (C_nH_{2n}) and acetylene series (C_nH_{2n-2}) of the open chain hydrocarbons are not present to any appreciable extent in bitumens, tars, or pitches (*cf.* gilsonite).

The cyclic saturated hydrocarbons (C_nH_{2n}) occur largely in Russian (Baku) petroleum, in asphaltic petroleum (Ohio, California, Canada, and Colombia), and in Borneo petroleum. The first member

of the series is a gas (b.p. -35° C.), viz. trimethylene $CH_2 \begin{matrix} \nearrow CH_2 \\ \searrow CH_2 \end{matrix}$.

whereas cyclononane $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \\ | \\ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \end{array} \text{CH}_2$ is a liquid (b.p. 171°C .), which will give an idea as to the variation in volatility with change in molecular weight.

The cyclic unsaturated hydrocarbons may be represented by monocyclic cyclopentene $\begin{array}{c} \text{CH}_2-\text{CH} \\ | \quad \parallel \\ \text{CH}_2-\text{CH} \end{array}$, which occurs largely in Texas oils and in certain asphalts. A polycyclic saturated hydro-

carbon tricyclodecane $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2 \\ | \quad | \quad | \\ \text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2 \end{array} \text{CH}_2$ (m.p. 9°C .), a polymer of the above, is found in Texas, Californian, and Ohio petroleum.

The coal tars are essentially aromatic bodies of the $\text{C}_n\text{H}_{2n-6}$ series, with the attendant hydrocarbons of the naphthalene and anthracene series, together with phenols.

With reference to the varieties containing oxygen, sulphur, and nitrogen, nothing is known. Ammonia and pyridine are obtained by destructive distillation, but how they originated is unknown. The composition of petroleum and of tars has been extensively investigated, but comparatively little is known regarding the chemical composition of asphalts and coals. No two petroleum are alike in composition, and the same applies to asphalts, tars, and pitches. The simpler volatile and degradation products lend themselves to comparatively easy investigation.

The percentage of carbon varies between 84 and 94, whilst the hydrogen percentage lies between 8 and 15 (C_nH_{2n} series of hydrocarbons contain 85.7 per cent carbon and 14.3 per cent hydrogen).²

Asphalts.—With native asphalts associated with mineral matter the varnish maker is not concerned, so that mere mention of a few well-known asphalts of historical and general importance will be sufficient. The asphalts of Mesopotamia, containing 25 per cent of bitumen and 71 per cent of mineral matter, were used as early as 3000 B.C., and the asphalt of Hit is of similar antiquity. Trinidad asphalt contains 55 per cent of bitumen, 35.5 per cent of mineral matter, and 9.10 per cent of water of hydration. Val de Travers asphalt (Swiss) was first worked in 1112, and contains 10 per cent of bitumen. Syrian asphalt contains 25 per cent of bitumen. Oklahoma (U.S.A.) asphalt contains 12 per cent of bitumen in sand. The refining of the above for special purposes is generally too expensive, and for varnish-making purposes freedom from mineral matter is of special importance.

The estimated annual consumption of asphalt for roofing in 1921 was 625,000 tons; for paving, 669,000 tons; for waterproofing, flooring, insulating compounds, and varnishes, 144,000 tons.³ Bermudez asphalt (Venezuela) was first obtained in 1891 from a pitch lake similar to the famous Trinidad asphalt lake, although it was mentioned by Sir Walter Raleigh in his book *Discoveries of*

Guiana, 1595. It constitutes one of the largest deposits of pure asphalt, containing mineral matter up to $6\frac{1}{2}$ per cent. For varnish making its hardness does not equal that of the more popular asphaltites.

Trinidad manjak is obtained from two mines situated about ten miles from the famous asphalt lake. It is almost pure bitumen, like coal in appearance, hard, brittle, and odourless. The manjak is found in long seams between layers of clay, and is mined down to a 37-ft. seam at a 400-ft. level. The export of crude manjak is not profitable, but by compounding it with mineral oil the special preparations can be sold at a profit. It is boiled locally with oils at high temperatures and made into rust-preventative coatings of all kinds for boilers, pipe lines, etc., which are most effective in hot and damp climates. It often closely resembles Barbados glance pitch and gilsonite, according to the part of the vein from which the sample is taken.

Abraham ⁴ groups the asphaltites into three classes: gilsonite, glance pitch, and grahamite. Since all are presumably derived from the metamorphosis of petroleum, the classes will merge into each other:

	Streak.	Specific Gravity.	Fusibility.	Per-centage Solubility in 88° Naphtha.	Per-centage of Saturated Hydrocarbons.
Gilsonite . .	Brown	1.05-1.10	250°-350° F.	40-60	5-5
Grahamite . .	Black	1.15-2.20	350°-600° F.	0-50	0-3
Glance pitch or manjak	Black	1.10-1.15	250°-350° F.	20-50	..
Bernudez asphalt	Brown to black	0.95-1.12	60°-325° F.	25-95	..
Impsonite . .	Black	1.10-1.25	Infusible	Trace	Trace

The percentages of fixed carbon are: gilsonite, 10-20; grahamite, 30-35; glance pitch or manjak, 20-30; impsomite, 50-85.

The importance of the solubility in 88° Bc. naphtha (s.g. 0.642) will be referred to later under the Examination of Pitches. The harder the pitch, the smaller the percentage soluble in 88° Bc. naphtha. The soluble portion contains petrolenes or malthenes, whereas the insoluble portion contains asphaltenes. Coal-tar pitches are relatively insoluble in 88° Bc. naphtha. Marcusson ⁵ recognises the presence in natural asphalts of: (1) oily substances (saturated and unsaturated hydrocarbons): (2) petroleum resins, which form the first stages of conversion of the petroleum hydrocarbons into asphaltenes. They are brownish-black substances soluble in petroleum spirit, chloroform, and carbon disulphide: (3) asphaltenes, formed by the action of oxygen or sulphur on the resins or by intramolecular change of the resins themselves. They are completely soluble in carbon disulphide, benzol, and chloroform, and contain

7.13 per cent of sulphur : (4) asphaltogenic acids and their anhydrides ; these are tar or resinous substances, soluble in chloroform or ethyl alcohol. The percentage of free carbon represents a coking value, and is useful in differentiating asphaltites from asphaltic pyrobitumens and non-asphaltic pyrobitumens. The percentage of saturated hydrocarbons represents the part insoluble in fuming sulphuric acid.⁵

Gilsonite.—This asphaltite occurs only in Utah in a number of parallel veins varying from fissures to several feet in thickness (18 ft. Cowboy Mine). Near the outcrop it loses its brilliant lustre, changing to a dull black due to weathering. Along the veins it shows a columnar structure extending at right angles to the walls, which is characteristic of asphaltites. The veins occur in sandstone and shale, so that gilsonite impregnates the walls and the line of demarcation is indefinite.

The methods of mining are simple, and little timbering is required as the veins are nearly vertical with firm surrounding rock. Twenty thousand tons have been mined and shipped from the region, and it is estimated that 32 million tons are yet available. Utah gilsonite on distillation under reduced pressure yields members of the C_nH_{2n} and C_nH_{2n-2} series resembling the hydrocarbons in petroleum ; moreover, it contains the same nitrogen compounds as petroleum. There is evidence of gilsonite being of organic origin. Grahamite gives a series of hydrocarbon resembling those from gilsonite.⁷

Glance Pitch.—This asphaltite appears to be intermediate between the native asphalts and grahamite. There are several varieties from Mexico, Barbados, Colombia, Syria, and the Dead Sea. Only those from Barbados and Colombia are used in the manufacture of varnishes and japans. In Barbados it was discovered in 1750 and has been worked since 1896. Near the surface Barbados manjak is hard and brittle with a high fusion point, but at lower levels of the mine it is softer with a lower fusion point, and is more like an asphalt than an asphaltite. It contains 0.7-0.9 per cent sulphur and 1.2 per cent mineral matter. In the United States Barbados manjak holds a unique position in the manufacture of insulating varnishes and other high-grade coatings. It carries three times as much oil or thinning medium as a similar weight of American gilsonite or Mexican bitumen.⁸ The Colombian variety contains 3.3 per cent mineral matter and has a fusion point of about 275° F.

There are large veins of asphalt at the bottom of the Dead Sea, and as it becomes detached from the bottom, presumably by earth movements, masses of asphalt rise and float on the surface of the lake, the water of which has the high specific gravity of 1.21. The supply is limited and the material is used only to a small extent locally. The deposit is merely of historical interest, as it formed one of the most important sources of supply for the ancients.

Grahamite.—This asphaltite is mined in Oklahoma, occurring in a fault or series of faults in shaly sandstone. The veins dip at an angle of between 45° and 50° and are from 19-25 ft. thick. The

asphaltite near the wall of the seam shows a hackly structure and is dull, whereas in the centre of the vein grahamite shows a conchoidal fracture and very bright lustre. The mine is now nearly exhausted.

Impsonite.—The final stage of hardness and infusibility of the bitumen asphalts is shown in impsonite (Oklahoma). It is almost insoluble in carbon disulphide and contains a high percentage of fixed carbon, but comparatively small percentage of oxygen (less than 5 per cent). Outcrops of grahamite are prone to weather to impsonite, which represents the final stage in the metamorphosis of asphaltites. Impsonite will not fuse alone, but must be blended with other pitches, and not more than 20 per cent can be incorporated with gilsonite to melt at 500°-525° F. Impsonite gives a black stain, so that a blend with gilsonite reduces the brown stain of the latter pitch.

Petroleum Pitches.—Closely allied to the natural bitumens and asphalts are the residuals from the distillation of asphaltic petroleum. Abraham⁴ states that there are two types of petroleums with intermediate groups: (1) non-asphaltic petroleums which contain open chain hydrocarbons and solid paraffin, but yield no asphalt. Sulphur and nitrogen may or may not be present; (2) asphaltic petroleums containing cyclic hydrocarbons, no solid paraffins, and yielding asphalt. Sulphur and nitrogen are generally present. Petroleum pitches are jet black lustrous solids, often brittle, with a conchoidal fracture and a low ash content (0.1 per cent). With the exception of the Mexican residuals they contain only small amounts of sulphur, so that they are in marked contrast in these two respects to the natural asphalts. In the early days of the industry the residual asphalts were carelessly manufactured without suitable temperature control. Now they are of excellent quality, including products fusing as high as 225° F., with satisfactory hardness and no greasy surface on ageing. There are wide variations in specific gravity and fusion point. The distillation of the petroleum is continued very carefully, not above 650°-700° F., until the residual asphalt acquires the desired grade.

	S.G.	F.P.	Ash.	Fixed Carbon.	Sulphur.	Solubility in		Saturated Hydrocarbons.
						CN ₂ .	88° Naphtha.	
Californian pitch	1.03-27	105°-220° F.	0.05-1	12-37	0	98-6-99	52-82	30
Mexican pitch	1.015	140°-160° F.	0.05-2	29-32	4-6	97.5-98	62-76	30-40
Trinidad petroleum pitch	1.15-1.20	132°-210° F.	0.5-1.28	29-38	2.2-2.8	99.3	66-78	24-28

Richardson⁹ states that the greater the percentage of saturated hydrocarbons the more pronounced are the asphaltic characters, which is borne out by service tests. Blown petroleum asphalts

are obtained by blowing air and steam through petroleum, freed from illuminating oils, at 525°-575° F., until the residue attains the desired consistency due to polymerisation and dehydrogenation. These are not used by the varnish maker.

The residual petroleum pitches may be distinguished from the asphaltites by lower fusion point, lower ash content, percentage of saturated hydrocarbons above 25 per cent (native asphalts contain 25 per cent, asphaltites less than 10 per cent), percentage of asphaltous acids below 2½ per cent and asphaltous anhydrides below 1½ per cent, whereas native asphalts have much higher value.¹⁰ The proportion of oily constituents is much greater than in the natural asphalts. The residues from some of the American petroleum contain aromatic hydrocarbons, *e.g.* anthracene, etc. The petroleum pitches are easily soluble in benzol and carbon disulphide, but are insoluble in water, acids, and alkalis. They are quite waterproof and resistant to extremes of temperature, are free from ash, and make good elastic black lacquers for iron work and for ordinary bituminous paints. It is stated that the residual asphalts are inferior in weather-resisting properties to the native asphalts and fatty acid pitches of the same fusion point and volatility, but they are superior to those obtained from rosin, lignite, and wood. The first-grade petroleum bitumens, natural and artificial, make good elastic coatings suitable for electric cable insulations,¹¹ or for electric cable trenches when incorporated with kaolin.¹² Toch points out that some asphalts are unsuited for making bituminous paints, because, under the influence of light, moisture, and atmospheric oxygen, oxidation of the hydrocarbons (polymethylenes) occurs, with the production of fine particles of carbon.

The U.S. Navy Department specification for petroleum pitch requires a black wax-like residue of pure bitumen resulting from the distillation of an asphaltic-base petroleum. The specific gravity must be 1.02 (15° C.), fusion point (Barrett method) about 203° F., and it must be completely soluble in petroleum spirit and mineral oil.)

Ozokerite.—Among the mineral pitches Galician ozokerite, after distillation of the volatile petroleum, gives a hard waxy substance, breaking with a rough granular fracture. In colour it is dark amber, softening at 50° C. and melting between 85° and 100° C. Ozokerite and ceresin (the product obtained by refining ozokerite with concentrated sulphuric acid) are employed as "finishing wax" and in electric cables. Some qualities burnish well and take a high polish. They are easily soluble in turpentine, carbon disulphide, petroleum, and benzol, but not in alcohol.¹³

Stearine Pitches.—Stearine pitches are the residues remaining in the still after the distillation of fatty material or white fatty acids in superheated steam under ordinary pressure or under reduced pressure. They are of value for blending with natural bitumen, as they possess high lustre, satisfactory hardness, elasticity, and complete or partial solubility in turpentine or petroleum.

The 'pitches from drying and semi-drying oils are less soluble in the above solvents.¹⁴

Fatty acid pitches vary considerably in their chemical and physical properties, depending on :

(a) the nature of the fat or oil from which the fatty acids are derived ; from high melting point fatty acids solid or semi-solid pitches are obtained ;

(b) the proportion of natural fats present in the original fatty acid mixture ;

(c) the temperature of distillation.

The fatty acid pitches contain free fatty acids, their hydroxy-acids, lactones (anhydrides), undecomposed glycerides, and hydrocarbon decomposition products, which impart a black colour to the pitch. Holde and Marcusson¹⁵ state that high boiling point saturated and unsaturated hydrocarbons with asphaltic hydrocarbons are present.

Abraham states that the higher the percentage of saponifiable constituents the better the weather-resisting power, and that fatty acid pitches of the best quality contain not less than 90 per cent of saponifiable matter. They are as weather-resisting as any of the natural bitumens. The saponification values vary from 33 to 100 and above, whereas the petroleum asphalts do not exceed 21 and are generally 5-18. On the other hand, some fatty acid pitches may contain as much as 98 per cent of unsaponifiable matter and are of good opacity with a lustrous black colour, and are satisfactory for japans for inside work. The softer the pitch the higher is its iodine value and the greater the content of free fatty acids. The blackest pitches are the hardest. Medium soft whale-oil pitch is quite brown in colour. The hardening and toughening of stearine pitches on exposure to air is due to oxidation. They flux satisfactorily with gilsonite and glance pitches, but not with grahamite. The most useful properties are plasticity and high viscosity, which are imparted to their blends with other bitumens.¹⁶ The chief varieties are :

Stearine Pitches.—From lard, giving ductile pitches, and from tallow, which yields hard but not ductile pitches.

Palm Oil Pitches.—Hard, but lacking in ductility.

Cotton Seed Oil-foots Pitches (Black Grease).—Soft and of moderate ductility.

Corn Oil-foots Pitches.—Rubbery, only slightly soluble in carbon disulphide, and possessing little ductility.

Wool Grease Pitches.—Ductile, with a black streak and containing cholesterol.

Special black varnishes for coating tarpaulins are prepared from fatty pitches, especially cotton seed pitch, as these substances yield plant surfaces, showing no tendency to crack, as is the case with some soft mineral oil pitches. The articles may be dipped in the melted soft pitch, or a solution of it in a suitable solvent, and stoved at 150°-350° C. In combination with paraffin oil, wood tar, and other materials, stearine pitches have been used

for the manufacture of special black or dark-coloured printing inks.

	Lard.	Tallow	Cotton Seed.	Palm Oil.	Wool Grease.	Whale Oil.
Fracture	conchoidal	..	conchoidal
Streak . .	brown	brown	brown	brown-black	black	brown
S.G. at 77° F.	1.00	1.06	0.95	0.98-1.08	1.02	1.016 (15° C.)
Susceptibility						
factor . .	12	22	15-19	29-41	36	..
Fixed carbon	12	18	9-10	26-34	30	..
Solubility in CS ₂	100	98.5	97-99	96-98	99	..
88° naphtha	98	87	92-100	82-92	99	..
Mineral matter	0	2.1	0.2-0.4	2.98	0.5	0.48
Saponification						
value	179	156	151	58.3	125	67.8
M.P. (K. and S.)*	110° F.	182° F.	70-100° F.	161-172° F.	91.5° F.	38° C.
Sulphonation re-						
sidue and sul-						
phur . .	0	0	0	0	0	0
Acid value	82	41	60	46-113	10.7	..
					per cent	
					oleic acid	
					126	..
Iodine value	118

* Krauer and Sarnow method page 170.

Bone Pitch.—Bone pitch is an intensely black pitch obtained in the distillation of bone oil (Dippel's oil) produced when bones are dry distilled. Bone oil yields 23 per cent of hard pitch. Bone-tar pitch is intermediate in its properties between asphalts and fatty acid pitches. It is not very soluble in solvents and is generally fluxed with more soluble pitches, to which it imparts a black shade. It is produced in comparatively small quantities.

Coal-tar Pitch.—Coal-tar pitch is the residue remaining in the still after the first distillation of coal tar, and forms about two-thirds of the weight of the treated tar or 4 per cent of the weight of the coal carbonised. For the varnish maker the use of coal-tar pitches is restricted by their very partial solubility in petroleum, although they are freely soluble in coal-tar spirit. Weiss¹⁷ points out in his review of the present knowledge of the composition, properties and uses of coal-tar pitches, that their character depends on (1) the character of the tar distilled, (2) the percentage of the total distillate removed.

The lower specific gravity tars produced at a carbonisation temperature of about 800° C. are rich in open chain paraffinoid bodies and give a lower yield of pitch than the high-gravity tars containing closed chain aromatic compounds with free carbon. A harder pitch is produced by heating strongly to obtain the maximum yield of anthracene distillate, and the residual pitch is graded by the addition of creosote or anthracene oil. Stewart¹⁸ states that at high temperatures and with light charges a yield of 78 per cent of pitch is obtained. Continual distillation from vertical retorts gives 47 per cent, whereas moderate heat and fairly heavy charges give 56 per cent of pitch of finer quality and a lower content of free carbon. Related to coal-tar pitch are coke- and blast-furnace pitches produced by the distillation of their respective

tars.¹⁹ Coal-tar pitches have the following characteristics: they give a jet-black streak on porcelain and show free carbon under the microscope. The specific gravity is comparatively high (1.2-1.3). The susceptibility factor is high, the pitches becoming brittle in winter and softening in the summer heat: moreover, they pass rapidly from the solid to the fluid state. In carbon disulphide they show a comparatively high percentage of insoluble material; they are insoluble (70-90 per cent) in petroleum naphtha. Soft coal-tar pitch softens at 37° C. and melts at 60° C., moderate hard pitch softens at 60° C. and melts at 80° C., whereas the hard variety softens at 80° C. and melts at 175° C. The melting point is taken, as the point at which the pitch becomes soft enough to flow.

Marcusson²⁰ considers that coal-tar pitch consists of insoluble carbonaceous substances, high molecular weight hydrocarbons, phenols, and resins with drying properties, besides compounds containing nitrogen and sulphur and free carbon. The insulating power is high, the specific resistance being so large that accurate measurements are impossible. When dissolved in the usual tar solvents, it comprises the main ingredient of the best tar paints, and its waterproofing property and power to adhere to stone, wood, and felt, and as cement for sealing joints in stoneware pipes, make it of great value. In a japan coal tar-pitch would impart tackiness to the film.

Brown coal, cannel coals and bituminous shales yield tars on destructive distillation, from which pitches allied to coal-tar pitch can be obtained. By the distillation of lignite a coal-tar is produced, consisting of oil and paraffin wax and very little asphaltic substances. The softer lignite pitch, which has an odour of strongly heated paraffin, is completely soluble in turpentine and benzol. It has good insulating properties when admixed with caoutchouc and similar substances. Lignite-tar pitch is distinguished from asphalt-resin pitch and fatty pitches by giving the diazo-reaction; from coal-tar pitch by its complete solubility in benzol and carbon disulphide; from wood-tar pitch by the presence of associated sulphur and paraffin wax. In Germany it is used extensively in the manufacture of cheap paints in consequence of its solubility in petroleum.

	M.P	Insolubility in Benzol.	Per cent Sulphur.	Iodine Value.
Lignite pitch .	86° C.	0	2.14	93.7
Coal-tar pitch .	91-92° C.	46	0.31	50.0
Wood-tar pitch .	195° C.	42	0	140.0
Wool-grease pitch	32° C.	0	0	36.9
Stearine pitch .	48° C. †	0	0.67	40.4
Petroleum pitch	126° C.	4	1.00	103.5

Stockholm Pitch.—Stockholm or Swedish pitch and rosin pitch are typical products of the distillation of wood tar and of rosin

respectively. Stockholm tar is a peasant-made wood tar from the roots of *Pinus sylvestris* by a process similar to that of charcoal burning. A pipe at the bottom of the pile built on a slope leads the tar to the collecting vessel.

The roots are not really burnt, but only sweated, and the fire must be carefully controlled. The work is hardly remunerative, considering the risks taken. Stockholm tar when distilled gives light oils (s.g. 0.84-0.88) and about a 70 per cent yield of pitch. The pitch is soft, with a jet-like lustre, but of brown colour in thin films. It is easily soluble in alkalies, owing to the presence of phenolic derivatives, e.g. methyl esters of the cresols and of trihydric phenols, and on this fact depend its antiseptic and preservative powers. It finds wide application in the painting of ships, in the preparation of black varnishes, in the rubber and gutta-percha trades, as insulating materials, and in the preparation of impermeable cements. The wood pitches are very susceptible to changes in temperature, possessing a low fusion point, but they are not weather-proof, being prone to oxidation on exposure to the weather, and thus becoming rapidly converted into a pulverent condition. Prior to 1914 the annual yield from Russian sources (Archangel) was estimated at 55,300 tons. The differences between the characteristics of pine pitches and hard wood pitches, and the contrast between these and coal-tar and petroleum pitches, are shown in a table given on preceding page.²¹

Rosin Pitch.—Rosin pitch is the residue left on the distillation of rosin (colophony), and amounts to 16 per cent of the rosin taken, the other products being rosin oil (67 per cent), pinoline or rosin spirits (3 per cent), and non-condensable gases (9 per cent). Rosin pitch resembles rosin in physical properties, possessing a rosin-like odour, sticky feel, and crumbling easily on slight pressure; moreover, it is yellow-brown in colour. It is very susceptible to temperature changes and does not withstand the action of the weather. Rosin pitch is rarely used alone in varnishes, and only occasionally when blended with low-grade pitches. Burgundy pitch is not a pitch, but an oleoresin. It contains more or less turpentine and emulsified water, and its composition is essentially that of rosin containing turps and water.

EXAMINATION OF PITCHES

It is evident, from the description of the bituminous substances, including pitches, that their identification is not easy: the detection and estimation of the components of a blended mixture are often very difficult. The most important tests in the examination of crude, refined, and blended bitumens are grouped under the following headings: Physical tests; colour, homogeneity, fracture, lustre, streak on porcelain, specific gravity, hardness or consistency, ductility, tensile strength, adhesiveness, susceptibility factor, and viscosity. The details of these tests are to be found in Abraham's

work, and a brief reference to the most important which concern the varnish maker will be sufficient.

Physical Tests.—*Hardness or Consistency.*—For the hardest bituminous materials Mohr's scale may be applied, whereas a needle penetrometer and a consistometer are used for semi-solids to moderately hard solids. The standard test for penetration of bituminous material is described in D. 4, *Am. Soc. Testing Materials*, 1918, 631. This test is used more frequently in America than in England. Penetration is defined as the consistency of a bituminous material expressed as the distance a standard needle vertically penetrates a sample of the material under known condition of loading, time and temperature. When the conditions of the tests are not specifically mentioned, the load, time, and temperature are understood to be 100 grams, 5 secs. and 77° F. respectively, and the units of penetration to indicate hundredths of a centimetre.

The consistometer²² registers the degrees of hardness on a scale ranging from 0-100, and may be used for determining the hardness of substances as soft as vaseline to substances as hard as gilsonite (100). In all cases the hardness is expressed as the cube root of the number of grams which must be applied to a circular flat surface 1 sq. cm. (100 sq. mm.) in area to cause it to displace a substance at a speed of 1 cm. per minute. The method of testing consists in forcing plungers of known diameter into the substance at the rate of 1 cm. per minute.

Fusion or Melting Point.—The softening of bituminous materials does not occur at any definite moment or temperature. With rise in temperature they change gradually from a brittle or soft material to a viscous liquid. The determination of the softening point must be made by a fixed, arbitrary, and closely defined method if the results are to be comparable. The methods proposed are many. The Kramer and Sarnow (K. and S.) method consists in heating a plug of the solidified bitumen, on which rests a small quantity of mercury, in a castor-oil bath provided with a thermometer, and the temperature at which the mercury drops through the plug of bituminous material is taken as the fusion temperature.

The ring and ball method consists in observing the temperature at which a steel ball falls through a ring which has been filled up by a plug of melted bitumen, the diameter of the ball being $\frac{3}{8}$ of an inch and the brass ring $\frac{3}{8}$ of an inch. Other methods are described by Mansbridge,²³ Fellows and Murphy,²⁴ and by Spielmann and Petrie.²⁵

Susceptibility Factor.—This factor is a numerical expression representing the susceptibility of a bituminous substance to temperature changes:

$$\text{Factor} = \frac{\text{Consistency at } 32^{\circ} \text{ F.} - \text{Consistency at } 115^{\circ} \text{ F.}}{\text{Fusion point (K. and S.)}} \times 100.$$

The more susceptible the material the higher will be the factor, which is of importance in the case of the softer pitches and tars. Asphalts have a susceptibility factor varying from 15 to greater than 100.

Solubility Tests.—*Solubility in Carbon Disulphide.*—In the case of native asphalts, the higher the percentage solubility in carbon disulphide the greater is their value. Crude bituminous materials are often purchased on the basis of percentage solubility in carbon disulphide, which indicates freedom from mineral matter. The details of the test are to be found in D. 4-11, *Am. Soc. for Testing Materials Standards*, 1916, 326.

Solubility in Petroleum Naphtha.—The harder the bituminous product the smaller is the percentage which will dissolve in 88° Bé. naphtha or in white spirit (s.g. 0.785-800). Coal-tar pitches are, however, relatively insoluble in petroleum naphtha. In the case of asphaltic pitches the insoluble part is termed "asphaltenes," whilst the soluble part comprises "petrolenes or malthenes." The solvent naphtha used in the test must be composed of open chain hydrocarbons, and 85 per cent should distil over between 95° and 150° F., because unsaturated or cyclic hydrocarbons exert a solvent action.²⁸

Chemical Tests.—Carbon, hydrogen, sulphur, and nitrogen are detected and estimated by the usual methods.²⁷

Saturated Hydrocarbons.—Richardson,²⁸ distinguishes between the various asphaltic substances (native asphalts, asphaltites, and petroleum asphalts) by estimating the saturated hydrocarbons, soluble in 88° Bé. naphtha, by means of sulphuric acid, which removes the unsaturated hydrocarbons.

Sulphonation Residue.—When a bituminous substance is heated, the distillate between 315° and 355° C. is sulphonated by sulphuric acid (80 per cent SO_3) at 98°-100° C. and the volume of the residue measured.²⁹ Gilsonite gives 85 per cent unsulphonated residue; wood-tar pitch, no residue; saponifiable and unsaponifiable fatty acid pitches also give no sulphonation residue, whereas residual asphalt from Mexican petroleum gives 86 per cent. The test expresses the percentage of saturated hydrocarbons in the distillate between 315° C. and 355° C.

Mineral Matter and Ash.—The ash content is determined by careful ignition of the material in an open platinum dish, until all the volatile matter has been expelled and the ignition carried to complete incineration.

Saponification Value.—Five grams of pitch in 25 c.c. of pure benzol are refluxed one hour with 25 c.c. of N. alcoholic potassium hydroxide, and after cooling, 200 c.c. 96 per cent of alcohol (neutralised) is added and the mixture titrated with $\frac{1}{2}$ N. hydrochloric acid, using phenolphthalein and alkali blue as indicators (3 c.c. of 1 per cent and 3 c.c. of a 3 per cent alcoholic solution respectively). The colour change is from a brownish red to a distinct blue.³⁰

Free Acids and Acid Value.—Five grams of the material and 50 c.c. of 96 per cent alcohol (neutralised) are boiled for twenty minutes under reflux, the alcohol is poured off and the residue digested again with alcohol, until the extract is no longer acid to alkali blue. The alcoholic extract is treated with 10 c.c. of 25 per cent barium chloride solution, 6 drops of alkali blue added and titrated cold with decinormal potassium hydroxide. The acids on

neutralisation give insoluble barium salts, which together with the unsaponifiable matter are dragged down, whereby the solution is cleared and the end point is more distinct.

Diazo-reaction.—This test is used for identifying bituminous substances containing phenols, including wood tar and wood tar pitch, peat and lignite tars and pitches, bone-tar pitch and various coal tar pitches. It depends on the identification of phenols by diazobenzolchloride.³¹

Liebermann - Storch Reaction.—This reaction may be used to detect the presence of rosin, rosin oil, and cholesterol. Rosin and rosin oil give a fugitive violet colour changing to brown. Cholesterol gives a fugitive rose colour changing to dark green. When all three are present the test is valueless. Other substances give definite colours in this reaction. Linseed, tung, and cotton seed oils give a greenish-brown coloration. Palm oil and olive oil give brownish yellow, and copals and fatty acid pitches give a permanent brown colour. The Liebermann-Storch reaction is most definite for the detection of rosin and rosin oil.*

Mansbridge³² gives a scheme for the examination and identification of pitches, which, however, does not apply to mixtures. It relies on a division into saponifiable and unsaponifiable bituminous substances and on the behaviour of the members of the two divisions to the solvent action of white spirit. In Section 1 the pitches, wholly or partly saponified, include stearine and wool-grease pitches and bone pitch. In Section 2 the pitches, which are unsaponifiable, include the natural asphaltums, ozokerite, pitches of the coal tar and mineral oil groups, and wood-tar pitch.

The solubility in white spirit of the pitches of Section 1 can be grouped as follows: completely soluble in white spirit are the stearine pitches from non-drying fats and wool-grease pitch, containing cholesterol. Pitches partially soluble in white spirit include the pitches from the drying and semi-drying oils and bone pitch. Insoluble in white spirit are the hard and elastic cotton seed pitches. The pitches of Section 2, which are soluble in white spirit, are the soft mineral oil pitches and the natural asphaltums. Partly soluble in white spirit are the mineral oil pitches, Trinidad, and natural asphaltums containing mineral matter and ozokerite pitch. Insoluble in white spirit and also unsaponifiable are wood tar pitch, a few mineral oil pitches giving an asphaltum smell when heated, and coal-tar pitches.

J. M. Weiss³³ has put forward a scheme of analysis of distilled tars and pitches, and E. C. Pailler³⁴ points out the differences between natural and oil asphalt, based on the estimation of the fixed carbon, on the acidity of the liquid obtained on careful dry distillation and on the saponification value:

Fixed carbon	9.95-16.87
Acidity	0.12-15.9
Saponification value	7.4-36

* Rosin can be extracted from pitch by means of alcohol if it is desired to estimate it.

J. Marcusson³⁵ also gives methods of detection of various pitches (natural asphalt, fat distillation residues, commercial products manufactured therefrom and coal-tar pitches) in the presence of each other.

In the examination of a black japan the pitch to be identified belongs to the class soluble in white spirit. In the ordinary scheme of varnish analysis the unsaponifiable part would contain the natural asphaltums and the mineral oil pitches. In the examination of the unsaponifiable portion the percentage of asphaltenes and their fixed carbon values will give an indication as to the character of the pitches, although it is not possible to estimate with any accuracy the components of a mixture of natural and petroleum asphaltums.

The saponifiable part and that soluble in white spirit will appear among the oil and resin acids in the ordinary method of separation, so that it is difficult to distinguish them in the presence of the resins and drying oils which go to make up the black japan. Some details of the examination of black japans will be given in the chapter on Analysis of Varnishes, and reference may be made to Gardner and Schaeffer, *Analysis of Paints*, 1911, and to C. D. Holley, *Paint Vehicles, etc.*, 1920.

Origin of Petroleum and Bituminous Substances.—The discussion of the origin of petroleum and bituminous substances is outside the sphere of this work, but a brief statement of some of the important theories put forward will be of interest. H. Abraham (*Asphalts and Asphaltic Substances*, 1921) classifies the theories under Inorganic, Vegetable, and Animal theories.

Inorganic Theories.—The decomposition of the metallic carbides in the earth's crust by water to give hydrocarbons is problematic, especially as no carbides have been found to be native. Another suggestion is that carbon dioxide acts on alkali metals at the high temperatures beneath the surface to give hydrocarbons, and a third suggestion is that hydrocarbons existed in the primordial atmosphere and that these condensed in the earth's crust when it cooled; this has the support of the fact that hydrocarbons have been detected in meteorites.

Vegetable Theories.—According to these theories bituminous substances are derived from deposits of vegetable matter, either terrestrial or marine. The optical activity of certain petroleum has been cited to substantiate this view, because hydrocarbons obtained from inorganic substances do not exhibit optical activity.

Animal Theories.—Bituminous substances are said to be derived from the accumulation of animal matter in the ocean depths, which is decomposed in time into hydrocarbons. Animal fats can yield pitches, and their conversion into petroleum is said to depend on three factors, viz. pressure, temperature, and time.

The vegetable and animal theories point to the presence of bitumens and pyrobitumens in rocks of a sedimentary character. It is probable that their origin may be accounted for by two or more of the theories given above.

Richardson³⁶ suggests that petroleum pitches originate by

surface action between natural gases and the sands with which they come in contact, and that asphalts are formed by the surface action of colloidal clays on heavy petroleum. Peckham³⁷ from a study of Californian bitumen considers that the polymerisation of petroleum and its conversion into asphalt are largely due to the presence of nitrogen and sulphur. A. Pictet³⁸ obtained by distillation of coal at 10-15 mm. pressure a mixture of hydro-aromatic hydrocarbons, homologues of cyclohexane and cyclohexadienes. At the temperature of ordinary gas retorts the vacuum pitch passed to ordinary pitch. The products obtained were identical with those contained in Canadian and Californian oil. By vacuum distillation of fats and soaps, mixtures of aliphatic hydrocarbons were obtained, such as are contained in Pennsylvanian petroleum.

The results of these experiments support Engler's theory of petroleum formation from animal residues and establish a distinction between aliphatic and cyclic petroleum in their respective animal and vegetable origin.

Sabatier and Senderens have produced petroleum oils by hydrogenating acetylene at high temperatures and pressures and W. Ramsay³⁹ has found traces of nickel in crude petroleum oils.

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CHAPTER XI

VARNISH SOLVENTS

Turpentine.—The oleoresin obtained, either by the tapping process, when the variety of the tree allows it, or from the wood, as in the production of wood turpentine, gives on distillation a volatile spirit, which is spirits of turpentine or turpentine oil. The non-volatile product (rosin, colophonium) has already been described. The turpentine used in Europe is obtained from (1) the United States (*Pinus palustris*, the Southern long-leaved pine; *Pinus taeda*, the loblolly pine; *Pinus caribaea*, the Cuban or slash pine); (2) France (*Pinus maritima* or pinaster); and (3) Russia (*Pinus sylvestris*, Scotch fir or Norway pine), with smaller quantities from Spain (*Pinus maritima*), Portugal (*Pinus maritima*), Algeria (Aleppo pine, *Pinus halepensis*), and Greece. Russia is the only country which can largely increase its output in the future, although the present output of turpentine and rosin from the United States is three or four times as great as that of France, Spain, and Russia together. The world's production of turpentine and rosin annually prior to 1914 was 850,000 barrels of spirits of turpentine, *i.e.* 42,500,000 galls., and 2,750,000 barrels of rosin of 500 lb. each. Of this huge amount the U.S.A. supplied 650,000 barrels of turps and 2,150,000 barrels of rosin. France supplied 130,000 barrels of turpentine, Spain and Portugal 50,000 barrels, Greece 15,000 barrels, India 2500 barrels, other sources 2500 barrels, all turpentine.¹ Central America is yet an undeveloped area, but turpentine is obtained from Mexico (Mexican White Pine, *Pinus ayacahuite*, and the slash pine, *Pinus caribaea*) and British Honduras. Within the British Empire Honduras and India possess pines (*Pinus longifolia*, the Chir pine, and *Pinus excelsa*, Himalayan or Bhotani pine) which yield a flowing oleoresin, but in India the industry has been developed as yet only for the home market. Eldridge² states that France will expand its production of oleoresin. Spain, Portugal, and Greece will remain stationary. Mexico and Central America may become important producers, but the output from India is not expected to exceed 37,000 barrels (50 galls.) of turpentine and 100,000 barrels (500 lb.) of rosin.³ It is stated that the supply of turpentine and rosin from the United States will cease in ten years' time, owing to the wasteful tapping of the trees which yield a flowing oleoresin. The

Douglas fir of the American Pacific littoral gives promise of exploitation. The progress of the wood turpentine industry is such as to justify the expectation that there will be an increase in the output of turpentine and rosin.

In the U.S.A., in 1920, 21,471,000 gallons of ordinary turps and 35,000 barrels of wood turps were produced, together with 1,452,000 barrels of rosin and 185,000 barrels of wood rosin. These figures show a diminution in production compared with the pre-war figures. It is estimated that the world requires annually about 50,000,000 galls. of turpentine and 1,500,000,000 lb. of rosin. It is evident that the "Naval Stores" industry is one of vast importance, and the production of turpentine and rosin requires careful attention. In the United States until the middle of last century the Carolinas were almost the sole source of supply of U.S. turpentine and rosin, obtained from the long-leaved pine. The area was extended to Georgia, Florida, Alabama, Mississippi, Texas, with Georgia predominant in 1900. In 1919 Florida, with 37 per cent of the total output, was the best.

The method of distillation is practically the same as it was fifty or sixty years ago, the apparatus consisting of a large copper kettle of 500-1000 galls. capacity connected by a removable still-head to a copper worm kept cool in a large tub of water. From 7 to 14 barrels of the gum are distilled in one operation. Some stills are made to hold 800 galls. (20-25 casks) of oleoresin and are fire heated so as to keep the oleoresin melted. Water comes over with turpentine at first, and afterwards a thin stream of lukewarm water is allowed to run into the still, so that the turpentine distils off in a current of steam at a temperature lower than its boiling point. When nearly all the turpentine has been distilled off, the flow of water is stopped, the still cap or head removed, and the molten rosin remaining in the still is drawn off through an opening at the bottom. The yield of turpentine varies from 16 to 22 per cent of the original weight of the oleoresin. The water and turpentine pass together into the receiver and are separated and removed at different levels by suitably inserted pipes. Each cask of turpentine is inspected for colour (water-white standard, one shade off, two shades off) and the barrels of rosin are tested for colour with samples taken 6 in. below the surface of the rosin in the barrel.⁴

Wood Turpentine.—*Kienöl, Pine-knot Turpentine.*—Turpentine may be obtained from the wood of the Douglas fir (*Pseudotsuga taxifolia*) by distillation in an electrically heated still. The products are turpentine, some rosin, pitch, and charcoal. Forty thousand pounds of wood give 7½ galls. turps, 18 galls. tar oil, 38 lb. rosin, 1338 lb. charcoal, and 20 lb. pitch.

Steam-distilled wood turpentine from the dead heart of the trunk and limbs is water-white and contains dipentene (b.p. 176° C.). By draining the fir pitch from holes bored into the tree turpentine and rosin can be obtained on steam distillation. When the flow of the fir pitch from the tree stops, the holes are plugged up so as to preserve the life of the tree. 'Live turpentine is obtained

from incisions in the living tree: *dead* turpentine from stems and roots of felled trees.

For the detection of wood turpentine in ordinary oleoresin turpentine colour tests are available, but the intensity of the coloration is no indication of the quantity of wood turpentine present. Herzfeld's test⁵ is to add 1 c.c. potassium hydroxide solution (s.g. 1.31) to 5 c.c. turpentine and warm on the water bath with vigorous shaking. If wood turpentine be present the spirit will be coloured brown, and if much is present a dark resin will separate out. It is advisable to perform a blank test with ordinary turpentine. Several other tests are recommended, which are described by H. Wollf.⁵

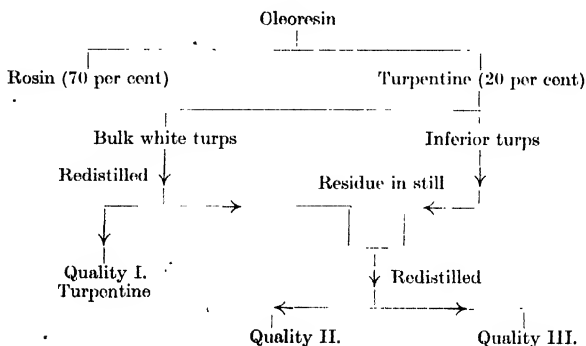
In America a mixture of turpentine and resinous bodies is obtained by the destructive distillation of coniferous wood, by steam distillation, or by extraction with solvents. In the case of the destructive distillation of wood the products consist of light oil, rosin oil, pitch, and a watery distillate which, on neutralisation with lime, gives calcium acetate and methyl alcohol, whilst charcoal is left in the retort. The process has been already referred to, and it is only necessary to describe the rectification and deodorisation of the oil. Its penetrating empyreumatic odour, contrasted with that of ordinary turpentine, makes it unsuitable for use. The smell can be much improved by rectification with lime water in the same manner as in the case of the copal oils. Schindelmeiser⁶ advises heating the crude wood turpentine under pressure (3 atmospheres) with aqueous ammonia at 140°-160° C. for several hours, whereby not only acids and phenols are removed, but also aldehydes and ketones. After washing with water and distillation in a current of steam a satisfactory turpentine is obtained. The components are sylvestrene, *d*-pinene, also dipentene, limonene, and terpineol.^{6a}

	Oleoresin Turpentine.	Steam-distilled Wood Turpentine.	Destructive-distilled Wood Turpentine. ⁷
S.G. (15.5 °C.)	0.8617-0.889	0.859-0.915	0.862-0.867
Colour	Water-white	Water-white	Colourless or very slightly yellowish, free from sharp penetrating odour.
η_D 20° C.	1.4684-1.4818	1.4673-1.4755	1.468-1.483 (15.5° C.)
n_D 20° C.	31.8 → 129.3	16.5 → 436.14	+34.4 → +77.6
Polymerisation residue	2 per cent.	2.5 per cent.	2.3 per cent.
Initial b.p.	1.4-159° C.	153-177° C.	143-160° C.
Below 170° C.	99 per cent.	95 per cent.	
Below 180° C.	88-99 per cent.	98 per cent.	180° C. 45 per cent.
Acid value	0-1	0.08	0.03
I.V. (Wijs, $\frac{1}{2}$ hour)	350-100	300-362	300-308

French Turpentine.—The French method of obtaining turpentine, which is the best developed at the present time, has been described under Oleoresins.

Indian Turpentine.—For details of the Indian method reference may be made to an article in *Naval Stores*, p. 201, by A. J. Gibson. The cultivation of the pine and the procedure of obtaining the

oleoresin from *Pinus longifolia* (Chir pine) and its subsequent treatment are conducted strictly on the French plan. The crude resin is melted and its specific gravity adjusted by addition of turpentine to allow the separation of water and dirt. Subsequent filtration by a gravity method and distillation on the French plan constitute the method of treatment.



Quality I. has a peculiar pleasant odour due to its components, Δ^3 -carene, a bicyclic terpene,^a and *d*-longifolene, a sesqui-terpene.

Turpentine and rosin are at present being produced in the United Provinces and Punjab.^{8a} The Punjab oleoresin is distilled at factories at Bhowali, Bareilly, and Jallo. The output of the Jallo factory is about 19,000 cwts. of rosin and 70,000 gallons of turpentine, which represent almost the maximum capacity of the factory. The maximum possible output from the Indian Government factories may be taken at about 73,000 cwts. of rosin and 300,000 gallons of turpentine per annum. The recent annual demand for rosin in India may be taken as 66,000 cwts., and the consumption of turpentine per annum has not exceeded 330,000 gallons, which confirms the statement made early in this chapter, that the industry can only supply the Indian market. The conclusion given in the Imperial Institute Trade Enquiry Report may be stated as follows: "Although at the moment there may be large supplies of rosin and turpentine owing to the shortage of shipping during the past few years, there is evidence that the area of pine forests in the United States is gradually being reduced and that production is declining. Further, the cost of production there has risen, owing largely to the increased cost of labour. The prices of American rosin and turpentine are therefore likely to remain high for some time, and there will consequently be a good market for the Indian products at high prices. Experiments should be continued with a view to the improvement of tapping of the trees and methods of collection of the crude oleoresin. Tank cars should be available for the conveyance of the crude oleoresin, and transport facilities should be improved in order that the total area tapped may be increased. If India

is to be in a position to make any noteworthy contribution to the supply of turpentine and rosin required by the United Kingdom and other parts of the Empire in the future, the Indian resin industry must be largely developed, especially in the direction of transport facilities in the forests. If the annual yield from all species of pine in India should amount ultimately to 440,000 cwts. of rosin and 1,600,000 galls. of turpentine, there should be an appreciable supply for export."

The peculiar odour of Indian turpentine will be a disadvantage in English and European markets, just as the French turpentine is often at a disadvantage compared with American turpentine, although the three varieties are equal as regards solvent properties and as varnish thinners. Simonsen (*loc. cit.*) ascribes to *d*-carene and longitolene the two properties of Indian turpentine which are considered to make it inferior to the American and French product, viz. ease of oxidation and higher percentage of residue on evaporation. *d*-carene readily absorbs oxygen from the air. Samples of Quality I. examined by the writer compared favourably with American and French turpentine in properties, differing only in odour.

Russian Turpentine.—The possibilities of obtaining large quantities of turpentine from Russia are great. The forests are immense. In European Russia 39 per cent of the area of the country is forest region and, including Siberia, it is estimated that there are 900 million acres of forest land. In Siberia the "taigas" consist essentially of pine, fir, spruce, and larch. The oleoresin can be obtained in some districts by tapping, but generally the wood is crudely distilled to yield turpentine and tar.

In the Archangel district 300,000 gallons of turps and 25,000 barrels of pitch (560 lb. per barrel), and 75-90,000 barrels of tar (32 gallons per barrel) were obtained annually before 1914. The destructive tapping of trees or the distillation of roots in brick ovens gives some turps and a light tar.

In the Kazan and Vjalka districts a crude distillation of the coniferous wood to give turpentine and tar is practised. In the Minsk area distillation of wood gives a yield of one-third turpentine and two-thirds tar (inferior to Archangel tar). Up to the present there has been a lack of initiative in the development, but wherever French methods have been tried the results have been promising. Poland and Lithuania are also turpentine-producing countries.

The imports of turpentine into the United Kingdom from Russia and Scandinavia in 1906 were 4139 cwts. or 16.4 per cent of the total imports. In 1914 they had fallen to 1210 cwts. or 6.95 per cent of the total imports, and in 1919 the imports were 562 cwts. or 2.47 per cent of the total imports.

Storage of Turpentine.—Iron tanks in which turpentine may be shipped or stored should not be galvanised, but should be coated with shellac. Investigations have shown that a persistent white turbidity in turpentine stored in galvanised iron tanks is due to finely divided zinc compounds held in suspension. A shellac coating.

instead of galvanising, prevents discoloration of the turpentine. The presence of water in the turpentine develops acids which dissolve the iron or the galvanising zinc. Any unshellacked iron surface will be attacked by turpentine in cold weather owing to separation of water from the spirit (*Decorator*, 1922).

Turpentine Hydrocarbons.—American turpentine contains α -pinene (dextrorotatory 80-85 per cent) and smaller quantities of β -pinene (nopinene), camphene, sylvestrene, and dipentene. The pinene from the Cuban pine is laevorotatory, but the preponderance of the long-leaf yellow pine accounts for the fact that American turpentine is generally dextrorotatory.

French turpentine contains α -pinene (laevorotatory).

The Cuban, or slash pine, also contains laevorotatory α -pinene.

Russian turpentine contains sylvestrene, which is dextrorotatory.

Indian turps contains: β -pinene (*l*-pinene), 60.8 per cent; *d*-carene, 14.8 (imparts a characteristic smell to the turpentine); *d*-longifolene, 10.2; residue and loss, 14.2 = 100.

Wallach and his pupils have made a careful study of the natural terpenes, and of late years a number of terpene hydrocarbons have been synthesised by W. H. Perkin, junr., so that their structural formulæ are fairly well established. In practice it is rarely necessary to isolate any of the characteristic derivatives of the terpenes, and the standards given below are adequate. The following is the American specification recommended for gum and wood turpentine, together with the characteristics of French and Russian turpentine:

	American Turpentine.	French Turpentine.	Russian Turpentine.
Specific gravity 15° C.	0.875-0.862	0.8725-0.870	0.8755
Flash point (Abel)	86°-88° F.	80°-88° F.	93° F.
n_D (20° C.)	1.478-1.468	1.4756	1.4760
Residue after polymerisation with 38N. H ₂ SO ₄ : Turpentine	2% (n_D 20° C. = 1.5)
Wood	2.5 (n_D 20° C. = 1.495)
Initial B.P. at 760 mm.: Turpentine	160° C.	155°-160° C.	..
Wood	150° C.
Percentage distilling below 160° C.	8
Percentage distilling below 170° C.	90	87.8-93.5	80-84

It must be remembered that pinene undergoes decomposition above 250° C. and gives resinous products, so that care has to be taken not to exceed that temperature during the dry distillation of wood.

The Terpenes.—The terpenes are ring compounds containing unsaturated linkages and asymmetric carbon atoms, so that the variety of their derivatives is great and their chemical activity is very marked.

[TABLE.

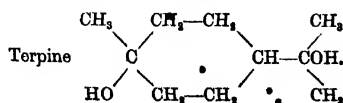
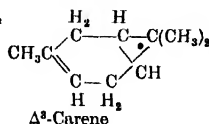
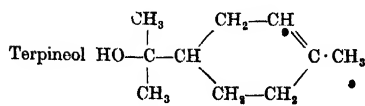
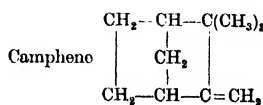
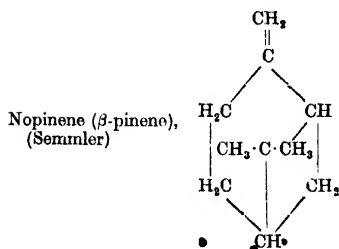
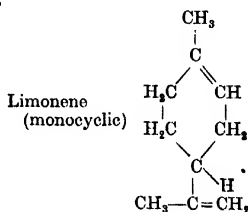
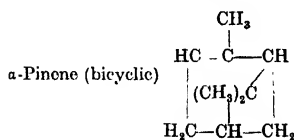
THE CONSTANTS OF THE TERPENES OF TURPENTINE

	B.P.	S.G.	α_D^{20} °C	Hydrochloride, etc.	Nitroschloride.
Pinene (a)	153.5°-154.5° C.	0.857/20° C.	-43°-48 (32°-0)	$C_{10}H_{16} \cdot HCl$ m.p. 125° C. $C_{10}H_{16} \cdot HBr$ m.p. 94° C.	$C_{10}H_{16} \cdot NOCl$ m.p. 115° C.
" (β)	103°-104° C.	0.8728/15° C.	-19°-8	$C_{10}H_{16} \cdot HBr$ m.p. 94° C.	..
Sylvestrene	177° C.	0.851	+66°-3	$C_{10}H_{16} \cdot 2HCl$ m.p. 72° C. $C_{10}H_{16} \cdot Br_2$ m.p. 135° C.	$C_{10}H_{16} \cdot NOCl$ m.p. 106°-107° C.
•	•	•	•	•	•
Limonene	175° C.	0.846	+106°-8	$C_{10}H_{16} \cdot Br_2$ m.p. 104° C. $C_{10}H_{16} \cdot 2HCl$ m.p. 50° C.	<i>l</i> -nitrosolimonene * $C_{10}H_{16} \cdot NO$
Dipentene (inactive Limonene)	176° C.	$C_{10}H_{16} \cdot Br_2$ m.p. 125° C.	..
Phellandrene	170°-172° C.	Nitrite m.p. 103°-104° C.	..
Camphene	161° (m.p. 50° C.)	$C_{10}H_{16} \cdot HCl$..

Pinene and camphene are bicyclic terpenes. Limonene and sylvestrene are monocyclic terpenes.

* Identical with Carvoxim.

The constitutional formulæ of:

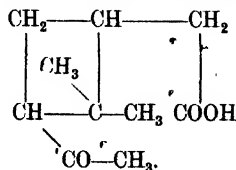


Veze⁹ has put forward a polarimetric method for determining the proportions of pinene and no-pinene in French turpentine.

General Properties of Turpentine.—The important general properties of turpentine which a varnish maker has to consider are (1) its solvent action, (2) its oxidation, (3) its polymerisation. Reference must be made to the production of synthetic camphor from turpentine (Luttringer and Dubose, *Bull. Soc. Ind.*, Rouen, 1920, 48, 84).

(1) *Solvent Action.*—Its solvent action on sweated and unsweated resins has been already dealt with. Turpentine is a ready solvent for vegetable drying oils and their metallic salts, and for the metallic resins. It mixes in all proportions with petroleum. It mixes with absolute alcohol and ether, but its solubility in water is small. Its viscosity renders it a superior "thinner" to white spirit, and its low volatility compared with the latter solvent allows greater freedom of working on the application of a varnish film. A characteristic smell combined with reliable solvent properties has given it a reputation, so that its presence in a varnish is deemed essential by some users. Its presence is indeed a decided advantage, but is not necessarily essential for all classes of work, because a blend with white spirit (suitably selected) will give a result almost equalling in many respects that in which turpentine is used alone. It must, however, be admitted that turpentine is the most reliable solvent, and is preferable, provided that its price is not prohibitive.* In some varnishes, *e.g.* insulating varnishes, it is a disadvantage owing to its chemical activity and its tendency to form copper salts when in contact with that metal.

(2) *Oxidation.*—When turpentine is exposed to air and light it evaporates and leaves a greasy residue (sobreol, pinol hydrate, $C_{10}H_{18}O_2$), as well as small quantities of cymene ($C_6H_4 \cdot CH_3 \cdot C_3H_7$), formic acid, acetic acid, and carbon dioxide. Another product of exposure of turpentine to air is camphoric acid aldehyde ($C_{10}H_{16}O_3$). In thirty days French turpentine will absorb 3.4 per cent of its weight of oxygen, whilst American turpentine absorbs 4.7 per cent with the production of 0.1 per cent carbon dioxide (Berthelot); nevertheless it is stated that French turpentine is more easily oxidised than American turpentine. It readily absorbs ozone to give an ozonide, decomposable by water and forming α -pinonic acid

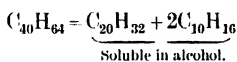


American and French turpentine evaporate easily at the ordinary

* Its low volatility may play a part in the maintenance of the surface of a varnish film after setting.

temperature, leaving a slightly greasy residue. Russian turpentine yields a much larger greasy residue, likewise crude wood turpentine, so that these two varieties are not considered to dry satisfactorily. No doubt during the evaporation of turpentine the greasy oxidation products may bind together the dissolved resin. Generally speaking, any catalytic oxidising powers may be considered small compared with those of drying oils.

(3) *Polymerisation*.—Sulphuric acid will polymerise turpentine to give colophene $C_{20}H_{32}$, a colourless oil with a bluish fluorescence (b.p. 300° – 315° C.). It is the formation of these polymers which are made use of in the analysis of turpentine. If antimony trichloride be used as polymerising agent, a solid substance, $C_{40}H_{64}$, is obtained, transparent and of a yellow colour (s.g. 0.977), which is insoluble in alcohol. On heating it depolymerises according to the scheme :



This change is illustrative of the depolymerisation ensuing in the sweating of resins. Turpentine absorbs bromine and chlorine very readily, and the bromine number of good turpentine is 215–230 ; iodine is not absorbed directly, but when it is made to react the terpene molecule is destroyed, with the production of hydriodic acid and other products.

An important change occurs when turpentine is heated with alcohol and dilute sulphuric acid ; a monocyclic terpene tertiary alcohol, terpineol (b.p. 110° C.) (*vide* p. 181) is obtained. Terpineol is a good solvent for resins, but its presence in varnish mixings encourages surface condensation and bloom (cf. Bloom). It has been synthesised, together with dipentene and terpine (a dihydric alcohol, $C_{10}H_{20}O_2$), by W. H. Perkin, junr., from a hexahydrobenzoic acid derivative.

With reference to the thermal decomposition of turpentine to yield isoprene, C_5H_8 , and toluene, S. A. Mahood¹⁰ states that the yield of isoprene from gum or wood turpentine does not exceed 5 per cent, and the conditions are not favourable to give remunerative quantities of isoprene and toluene for the preparation of synthetic rubber.

Estimation of Turpentine.—The great demand for turpentine and the variety of substitutes render necessary a careful control of the purity of the spirit. Each country has its own specification (often each Government department). The proposed specification by the U.S. Bureau of Chemistry has been given on p. 180. The British Standard Aircraft Specification (X. 21, July 1921) for turpentine for aircraft material is as follows :

Description.—The material shall be genuine refined turpentine of good colour, free from water and other visible impurities.

Residue.—The amount of residue determined by evaporating 10 c.c. in an evaporating dish (approximately 4 in. in diameter by $1\frac{1}{2}$ in. deep) on a bath of boiling water, and subsequently heating

for a period of two hours at 100° C. (212° F.), shall not exceed 2 per cent by weight, and shall be wholly organic and free from tackiness.

Specific Gravity.—The specific gravity 15.5° C. (60° F.) shall be not less than 0.860 and not more than 0.880.

Flash Point.—The flash point (Abel's close test) shall not be less than 90° F. (32° C.).

Distillation.—When 100 c.c. of the material are distilled in the standard distillation apparatus (British Standard Spec. 2D, 15) at a rate of 3.4 c.c. per minute, not less than 90 c.c. shall distil below 175° C. (347° F.) at 760 mm. pressure. The boiling point shall not be lower than 150° C. (302° F.), taken immediately after the collection of 1 per cent.*

Refractive Index.—The refractive index for the D. line shall be between 1.468 and 1.478 at a temperature of 20° C. (68° F.).

Polymerisation.—The amount of residue left after polymerisation shall not exceed 6 per cent, and its refractive index shall not be less than 1.50 at 20° C. (68° F.). The polymerisation test shall be carried out as follows:—40 c.c. of concentrated sulphuric acid (s.g. 1.84) shall be placed in a suitable graduated vessel and the whole immersed in iced water. 10 c.c. of turpentine shall then be added slowly and gradually mixed with the acid, care being taken that the temperature does not rise above 60° C. (140° F.). When the mixture no longer warms up on shaking, the whole shall be thoroughly agitated and the vessel placed in a water bath and heated to between 60° C. and 65° C. (140°–149° F.) for ten minutes, the contents being thoroughly mixed by shaking vigorously five or six times during this period. The vessel should be kept unstoppered during this operation. The vessel shall then be cooled to room temperature and allowed to stand for twelve hours. The residue shall be washed, the amount determined, and its refractive index taken.

This polymerisation method (Armstrong's) has been modified by the writer to overcome the difficulty of separation of the products when the turpentine sample contains white spirit.¹¹

Marcusson and Winterfeld¹¹ have put forward a method of estimating the amount of petroleum and aromatic hydrocarbons present in a sample of turpentine substitute containing turpentine. Into a 100 c.c. flask provided with a long neck, graduated in $\frac{1}{10}$ c.c., 30 c.c. of fuming nitric acid (s.g. 1.52) are poured and cooled to -15° C. by ice and salt. By means of a dropping funnel 10 c.c. of the turpentine under examination are allowed to drop very slowly into the nitric acid. The greater the quantity of petroleum spirit present, the quicker may the turpentine be introduced. About half an hour to one hour is required, according to the purity of the sample. The mixture is allowed to stand a quarter of an hour in the freezing mixture and the flask is filled up to the mark with concentrated nitric acid (not fuming), previously cooled to -10° C., until any solid separation has been driven out of the neck. The bulb must

* War Office Specification (1920, C.W.D. 408) for turpentine requires 70 per cent at or below 160° C. and not less than 90 per cent at or below 170° C.

remain the whole time in the freezing mixture to avoid secondary reactions. The volume of the residue (petroleum) is shown in the graduated part of the flask to about 2 per cent accuracy. The contents are now transferred to a separating funnel and the lower nitric-acid liquid is withdrawn and poured into 150 c.c. water. Evolution of heat occurs and more or less oil separates out, according to the amount of the petroleum spirit. The aqueous liquid is heated for a quarter of an hour on a boiling water bath and in a fume chamber to bring the resin from the turpentine completely into solution. After cooling, 100 c.c. ether are added, the water layer is withdrawn, and the ether solution is washed several times with water, then with 10 per cent of alcoholic potash (10 per cent alcohol), and finally with water. After drying the ether with calcium chloride, it is carefully distilled off and the residue weighed. The residue is a red-brown oil possessing the aromatic smell of nitro-compounds. The weight of the oil is divided by 1.15 to obtain the volume of the nitro-products of aromatic and cyclic hydrocarbons, and this volume is added to the volume of the oil insoluble in nitric-acid fluid obtained above.

The disadvantages of the method are the violent reaction with nitric acid and the use of ice, moreover, the separation of the benzol from petroleum is incomplete, owing to the solubility of the nitro-compounds in petroleum hydrocarbons, whilst many petroleum products contain appreciable amounts of aromatic hydrocarbons.

The polymerised product of turpentine is colophene and the volatile unpolymersed is cymene.

Another method for the estimation of turpentine has been put forward by Tausch,¹² which is based on the oxidation of turpentine by mercuric acetate. When pure turpentine is heated under a reflux condenser for three hours with mercuric acetate and methyl alcohol and then steam-distilled, no trace of turpentine is found in the distillate. The method may be used quantitatively, and the mercurous acetate formed may be collected, transformed into the chloride, and weighed. A blank experiment may be done with pure turpentine.

Salvaterra¹³ suggests three suitable methods for the estimation of oil of turpentine:

(1) Tausch's method, using mercuric oxide, 80 per cent acetic acid and methyl alcohol. The mixture is heated on a water bath for two or three hours and then steam-distilled.

(2) By the action of hydrobromic and bromic acids at 20°-25° C., whereby the turpentine is rendered non-volatile in steam. If wood turpentine (Kienöl) be present, it is advisable to use a little more hydrobromic acid. The method is unsuitable if tetrahydronaphthalene (tetraline) be present.

(3) By treatment of the spirit with iodine and mercuric chloride in alcohol, and keeping the mixture cool and in the dark for six hours. After addition of a concentrated solution of potassium iodide and excess of sodium thiosulphate, the solution is neutralised

and finally distilled in a current of steam. The volatile impurities in the turpentine are found in the distillate. By the first method wood turpentine to the extent of 10 per cent is volatile in steam, but not in the second and third methods.

For the detection and estimation of coal-tar oils reference may be made to a paper by Grotlisch and Smith.¹⁴

Pine Oil.—The term "pine oil" as now understood is the heavy oil obtained from the fractionation of crude steam-distilled wood turpentine. When the trunk, stumps, and roots of the pine have been allowed to remain on the ground for a number of years and are then steam-distilled, there are obtained certain heavier oils formed by oxidation and hydrolysis of the terpenes as the result of exposure to the atmosphere. To these heavier oils, which are volatile in steam, the term "pine oil" is properly applied. It is the intermediate product between turpentine and rosin obtained on the destructive or steam-distillation of pine wood, and is the heavy oil obtained on the fractionation of crude steam-distilled wood turpentine. Good quality pine oil has a pleasant aromatic odour, but when of inferior quality* it cannot be used for indoor work on account of the pernicious odour of the empyreumatic compounds which it contains. In paint or varnish mixings it flows out well under the brush, because of its comparative low volatility. It is a powerful solvent for resins and will hold them in solution in a varnish mixing. It has strong penetrating properties like solvent naphtha, and when used in an exterior paint serves to carry the pigment into the pores of the wood to produce a firm foundation coat.^{14a} Pine oil has the power of retaining a small quantity of water, and it is dehydrated with difficulty. It contains a high percentage of terpineol, $C_{10}H_{18}O$, from which terpine hydrate, $C_{20}H_{40}O_2 + H_2O$, can easily be obtained. Terpine hydrate is also a ready solvent for resins.¹⁵ Owing to the high-boiling fractions present in pine oil it is with difficulty removed from a paint or enamel by steam distillation.

WATER-WHITE PINE OIL

Specific gravity at 15.5° C., 0.9383.

Acid value, 0.27.

Iodine value, 124.4.

Flash point, 176° F.

Loss on heating on the water bath at 100° C. for 9 hours, 98.7 per cent.

Loss on evaporation at 65° F. (2 hours) 24.6 per cent, (32 hours) 90 per cent.

Fractional distillation at 100° C., 2 per cent; 174°-194° C., 7 per cent; 194°-205° C., 18 per cent; 205°-208° C., 28 per cent; 208°-210° C., 53 per cent; 210°-213° C., 88 per cent; 213°-216° C., 94 per cent; 216°-218° C., 98 per cent; 218° C., 99 per cent.

Ultimate analysis :	Carbon.	Hydrogen.	Oxygen.
Pine Oil	79	11.2	9.8
Terpineol requires	77.85	11.7	10.38
American Turpentine ($C_{10}H_{16}$)	87.7	12.1	..
Wood Turpentine	85.7	12.1	2.2

[TABLE.]

CONSTANTS OF VARIETIES OF TURPENTINE AND OF SOME TURPENTINE SUBSTITUTES

Constant	Portuguese Turps.	Spanish Turps.	French Turps.	Swedish Turps.	Russian Turps.	American Turps.	American Wool Turps.	Greek Turps.	Indian Turps.	Petroleum White Spirit.	Petroleum	Rectified Naphtha.
Specific gravity .	0.8655 80° C.	0.8690	0.858 15° C.	0.8585 15° C.	0.861 15° C.	0.863 15° C.	0.8592	0.8602 17° C.	0.862-0.871 15° C.	0.7755 15° C.	0.783 15° C.	0.880
Flash point	89° F.	91° F.	90.6° F.	93° F.	93° F.	80° F.	93° F.	83° F.	103° F.	75° F.	105° F.	70° F.
Fractionation— At 160° C.	..	88%	27.0%	13.5%	8%	38.5%	21%	(105° C.) 94.5%	° boiling below 170° C.	135° C. 4.5%	0.5%	135° C. 9.5%
At 170° C.	..	6.5%	67.75%	76.75%	65%	37.5%	31.5%	170° C.	80-90%	140° C. 3.0%	0.5%	140° C. 14.0%
Residue .	..	5.5%	4.25%	9.6%	27%	3.4%	17.0%	4.5%	..	145° C. 3.0%	5.3%	150° C. 21.0%
	155° C. 21.5%	31.0%	160° C. 35.5%
	170° C. 11.75%	33.5%	170° C. 11.75%
	200° C. 27.5%	38.0%	180° C. 12.5%
	Res. 8.25%	38.0%	Res. 16.0%

Turpentine Substitutes.—With the steadily rising price of turpentine and the prospect of shortage in America unless the cultivation of the pine forests in that country is methodically organised, it is only natural that substitutes for turpentine will be welcomed. The requirements for a good turpentine substitute are solvent power equal to that of turpentine and equally rapid air-drying, leaving little greasy non-volatile residue; the smell must be pleasant and resemble, as much as possible, that of turpentine; the flash point must be above 73° F. to conform with transport requirements. As far as possible, the rate of evaporation of the substitute must correspond with that of turpentine and, if the substitute be a blend, the less volatile components must have a solvent power for resins and oils equal to that of turpentine. This is a point which is often overlooked in the choice of a turpentine substitute, and has done much to render them unpopular. If the more volatile part of the substitute is a better solvent than the rest, then on its evaporation there may be left a film which is not homogeneous and may show pinholing and pitting due to separation of particles of the components of the varnish.

The basis of turpentine substitutes is essentially a petroleum blended with turpentine in varying amounts. If a petroleum could fulfil the above requirements, the use of turpentine would be unnecessary. The petroleum is generally not such good solvents for resin-oil mixings or metallic driers, nor have they the same viscosity and flow as turpentine. Certain natural petroleum have a solvent power as good as turpentine, but their thinning powers are greater, which is a disadvantage; moreover, when used in conjunction with other varieties of petroleum they are liable to defects already referred to, in that they are more volatile, with the result that pinhole structure of the film may appear.

The petroleum is so varied in composition that for comparison volatility tests only are carried out. Generally the presence of aromatic hydrocarbons tends to improve their solvent power. There would appear to be no definite evidence that turpentine assists the catalytic oxidation of the gum-oil mixing. It is also incorrect to state that any kind of turpentine substitute would cause "bloom" in varnishes. It is probable that the slight greasy residue of oxidised turpentine facilitates the retention of resin in solution in the film, because resins are more soluble in oxidised turpentine than in petroleum.

From the experience of the 1906 Test Fence of North Dakota Experimental Station,¹⁶ the substitution of petroleum for turpentine does not give the same results as where turpentine in moderate amounts is used. Friend (*loc. cit.*) found that, for paints on iron, turpentine and petroleum media are equal as to the durability of the coating.

White Spirit.—The specification for white spirit,¹⁷ given below, may be taken as the most recent for British requirements. This specification covers the requirements of white spirit for use as a turpentine substitute in thinning paints and varnishes.

Description.—The material shall be wholly a petroleum product. It shall be water-white, clear, free from water and other visible impurities; also free from objectionable odour.

Specific Gravity.—The specific gravity shall not exceed 0.800 at 60° F. (15.5° C.).

Flash Point.—The flash point (Abel's close test) shall not be less than 75° F. (24° C.).

Distillation.—When 100 c.c. of the standard material are distilled in the standard distillation apparatus (see British Standard Specification 21). 15) at a rate of 3.4 c.c. per minute, not less than 80 c.c. shall distil below 190° C. (374° F.), and not less than 90 per cent below 200° C. (392° F.) at 760 mm. pressure.*

Freedom from Grease.—No grease spot or mark shall be visible on the paper when 3 or 4 c.c. are allowed to fall on a sheet of ashless white filter paper, 20 cm. by 20 cm., and the paper is freely exposed to the air for one hour at a temperature not exceeding 60° F. (15.5° C.).

Residue.—The amount of residue determined by evaporating 50 c.c. in a shallow evaporating dish (approximately 4 in. in diameter by 1½ in. deep) on a bath of boiling water for a period of four hours shall not exceed 0.2 per cent by weight and shall be wholly organic.

Neutrality Test.—When 10 c.c. of the material are shaken with 10 c.c. of distilled water and methyl orange indicator is added to the aqueous layer, no acid reaction shall be shown, but when one drop of N/10 sulphuric acid is added the indicator shall show a permanent pink colour.

Freedom from Sulphuretted Hydrogen.—The material shall give no reaction for sulphuretted hydrogen when tested by the method described as follows:

Method for Testing for Sulphuretted Hydrogen.—50 c.c. of the material shall be shaken in a clean stoppered vessel with a small quantity of a solution of lead acetate. The lead acetate solution shall not become coloured.

The presence of sulphur or sulphides in a petroleum substitute may be detected by the copper strip test: Place a piece of polished sheet copper, 2 in. by ¾ in., in the bottom of an ordinary porcelain dish. Add 25 c.c. of the thinner under test and place the dish on an actively boiling steam-bath until the volatile part has disappeared. If the thinner contains elementary sulphur the copper will be coloured grey or black.¹⁸

Coffignier¹⁹ recommends the following fractionation values for white spirit:

	Per cent.		Per cent.
70°-100° C.	0.1	160°-170° C.	35.36
100°-130°	1.52	170°-180°	18.5.26
130°-140°	10.17.5	180°-190°	10.17
140°-150°	31.48	190°-200°	0.7
150°-160°	56.5.69		

A high-grade white spirit gives generally between 5 and 10 per

* War Office Specification (C.W.D. 406) for white spirit for use in paint and for cleaning shell requires 80 per cent distillate at or below 200° C.

cent non-volatile material above 200° C. (cf. *Standard Tests for Paint Thinners other than Turpentine*²⁰).

It will be evident that from the above figures the rate of evaporation will compare very unfavourably with that of turpentine on the application of varnish. If the thinner contains too high a percentage of light spirit there will be a tendency for the varnish to drag with the brush. In that respect tetraline has much to recommend it, as 4 per cent boils over between 150° and 200° C., and 96 per cent between 200° and 206° C. (f.p. 78° F.), but it is a slower spirit than turpentine. Borneo spirit containing aromatic hydrocarbons has a much more uniform fractionation, which improves as the percentage of xylol content increases. The estimation of the aromatic hydrocarbons can be effected by fuming sulphuric acid in which the paraffin hydrocarbons are insoluble.²¹

For the details of estimation of petroleum in turpentine further information can be obtained from Lunge and Keane, *Technical Methods of Chem. Analysis*, part i., vol. 3; also *Chem. Zeit.*, 1918, 42, 349, and Salvaterra (*loc. cit.*).

Solvent Naphthas.—These are fractions in the distillation of coal tars and consist of liquids containing solid hydrocarbons. Their odour and toxicity have limited their general use, except in special cases of stoving coatings. The fractionation range is very varied from that of benzol (s.g. 0.88, b.p. 81° C.), with toluol and xylol, to heavy benzol and solvent naphtha, boiling between 130° and 175° C.

	F.P.	Benzol.	Toluol.	Xylol.	Higher Homologues of Benzol.
Benzol (90 per cent) *	below 73° F.	84	13	3	..
Benzol (50 per cent) .	" "	43	46	11	..
Benzol (heavy) . .	above 73° F.	5	95
Solvent Naphtha	5	70 35	25 65

Coal-tar oil (s.g. 0.942) contains 66 per cent boiling between 80° and 160° C., with 20 per cent distilling over above that temperature, and leaving a solid residue.

For the estimation of xylol in solvent naphtha, Spielmann and Jones²¹ state that 100 c.c. solvent naphtha gave by their method 22.1 per cent (b.p. to 138° C.) and 69.7 c.c. between 138° and 170° C., i.e. 63 per cent xylol and paraffin, of which 8 per cent was shown to be paraffin, making the total percentage of xylene to be 55 per cent. The solvent properties of xylol are excellent, and although there is a prejudice against its general use in varnish making, no doubt this will be overcome if proper precautions are taken with respect to its blending and use, so that it promises to

* The term 90 per cent benzol means that 90 per cent of the spirit will distil over below 100° C.

be of value.¹ It is not advisable to apply it on undercoats which have not dried properly; otherwise its great solvent properties may soften them. There are, however, many other defects which arise from application of a varnish on a soft undercoat of paint or varnish. Due consideration must be taken of the deleterious effect of aromatic hydrocarbon vapours on the human system. According to some authorities the action of turpentine vapours is by no means innocuous, but this is not generally accepted.

It must be remembered that benzol products contain small quantities of thiophene (C_4H_4S) and carbon disulphide. For the detection and estimation of sulphur in petroleum see Marcussen²² and Herzfeld.²³ Francis and Crawford²⁴ state that the best method of detection of sulphur compounds in petroleum is by heating with sodium, and after treatment with water and neutralisation with hydrochloric acid, the addition of *p*-aminodimethylaniline sulphate and ferric chloride gives methylene blue. Fusion with sodium peroxide is stated to give accurate quantitative results, but B. Blount²⁵ considers that estimation by the Carius method is the most reliable.

Coal-tar oil contains, in addition to benzol with its homologues, naphthalene and tar spirit.

Tar Spirit.—Tar spirit is a valuable solvent spirit in black stoving japans, because of its power to hold in solution polymerised resins, oils, and metallic driers. Its colour, unpleasant smell, and low volatility render it undesirable in air-drying varnishes. It is obtained from the middle or creosote oils in the distillation of coal tar, and is essentially of a phenolic character. Its composition is very variable. The specific gravity may vary between 0.94 and 1.037, and its acidity between 27 and 116. On distillation a sample of tar spirit may give 18.25 per cent distilling over below 180° C. with a specific gravity of 0.86. Below 270° C. 54.5 per cent may distil over with a specific gravity 0.93, leaving a residue of a viscous liquid amounting to about 20 per cent. 'The acidity is sometimes reduced by treatment with alkali before being employed as a solvent in a black japan.'

Tetraline.—By the hydration of naphthalene at 150° C. with a nickel and copper oxide catalyser, fluid hydrides of the hydrocarbon are produced. Tetraline ($C_{10}H_{12}$), the tetrahydride of naphthalene ($C_{10}H_8$), has a s.g. (15° C.) 0.977, b.p. 150°–206° C., and f.p. 78° C., with 4 per cent distilling over between 150° and 200° C., and 96 per cent from 200° to 206° C.* Blended with petroleum and turpentine, it gives a substitute which is satisfactory for colours and yields a hard film.²⁶ Tetraline has been recommended in Germany as a turpentine substitute.²⁷ (It is stated that 20,000 tons of tetraline were used in Germany in 1920, largely as a substitute for turpentine in boot polishes.) A disadvantage of tetraline is that when used in white enamels a reddish discoloration is produced in the film, which is not due solely to the presence of a basic white pigment, although it is not so marked when lithopone is used. The cause is said to be due

* The absorption of oxygen proceeds rapidly in the presence of basic substances.

to the oxidation of the resin present, and retardation of the drying of the film seems to inhibit its occurrence. Zinc oxide enamels may be thinned with tetraline, if not too much resin is present, and if the oil has been previously treated so that it will dry to a hard glossy film without containing resin.²⁸ Another cause may be the oxidation of manganese driers in the presence of tetraline to give traces of a pink manganese compound. Owing to its solvent action on linoloxyn it will soften undercoats of paint or varnish.

Dekaline.—The dekahydride of naphthalene, dekaline, has been put forward as a turpentine substitute.

Dekaline ($C_{10}H_{18}$) resembles turpentine in its properties more than tetraline. It evaporates more rapidly than tetraline; it does not dissolve linoloxyn and does not cause any softening of the undercoat. There is no reddish discoloration when used in white enamels. It dries more slowly than turpentine and possesses a camphoraceous odour. A mixture of 70 per cent of turpentine and 30 per cent of dekaline possesses the smell of turpentine. At present tetraline and dekaline must be looked upon as war substitutes, as their prices are too high, except in Germany, to compete with American or French turpentine. The solvent properties of tetraline and dekaline for resins and oils are better than turpentine,²⁹ although it is stated that dekaline is practically equivalent to turpentine in solvent power. E. Meier³⁰ gives the following comparison of tetraline, dekaline, and turpentine :

	Specific Gravity.	Flash Point.	Evaporation per minute.
Tetraline, b.p. 205°-207° C.	0.975	78° C.	0.14 per cent
Dekaline, b.p. 185° C.	0.900	60° C.	0.58 per cent
Turpentine	0.87	32° C.	0.58 per cent *

* Compare also S. Smith, *Chem. Trades Journ.*, 1920, 253, and N. Heaton, *Journ. Oil and Col. Chem. Assoc.*, 1923, 39, No. 39.

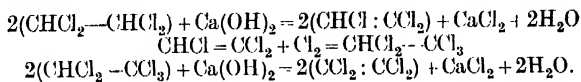
* Price in Germany, 31/3/22, 19.30 M. per kg. Both dekaline and tetraline are largely used in boot polishes. A mixture of tetraline and dekaline (1:4) is known as tetraline extra.

Other Varnish Solvents.—Mention must be made of a number of other liquids which are used as varnish thinners. Methyl and ethyl alcohols, ether, acetone, and carbon tetrachloride have been already referred to, and in connection with cellulose varnishes a series of alcohols, butyl alcohol, amyl alcohol (fusel oil), and esters, e.g. methyl formate and amyl acetate, will be discussed later. None of the above are used in oil varnishes.

Chlorinated Hydrocarbons.—Recently a series of chlorine derivatives of ethane and ethylene have found limited use in certain varnishes, because of their good solvent properties and their inflammable and non-explosive vapours. They have been employed as dope solvents, but the slow poisonous action of their vapours has made it impossible to continue their use.

		B.P.	Sp. Gravity.
Dichlorethylene	$C_2H_2Cl_2$	55° C.	1.25
Trichlorethylene	C_2HCl_3	88° C.	1.47
Tetrachlorethane	$C_2H_4Cl_4$	147° C.	1.60
Tetrachlorethylene	C_2Cl_4	121° C.	1.62
Pentachlorethane (Pentaline)	C_2HCl_5	159° C.	1.70

Tetrachlorethane is obtained by the action of chlorine on acetylene in the presence of antimony pentachloride. The union of chlorine with acetylene is never free from danger, and the acetylene and antimony pentachloride compound is treated with chlorine and acetylene alternately.³¹ The other chlorine derivatives are formed by the action of slaked lime on tetrachlorethane or by further chlorination.



Their action on metals is described by Gowing-Scopes.³² Dichlorethylene appears to have the least action, but in the presence of water its action is stimulated owing to the production of hydrochloric acid. The same author shows that resins are not easily soluble in these chlor-derivatives.

	$C_2H_2Cl_4$	C_2HCl_5	$C_2H_4Cl_4$	C_2HCl_3	C_2Cl_4
Rosin	very sol.	very sol.	sol. up to 7%	sol. to 7%	only 1%
Copal	up to 7%	1%	insol.	up to 7%	up to 7%
Kauri	20%	1%	1%	1%	1%
Dammar	20%	7%	20%	20%	20%

They would be of little use in oil varnishes, and present no great superiority, with only a few exceptions, over cheaper and harmless solvents. They are good solvents for acetyl celluloses.

Monochlor- (b.p. 132° C.) and *dichlorbenzol* (b.p. 172°-179° C.) have been proposed as special solvents, but their strong physiological action is unfavourable. They are stated to give slightly matt films in spirit varnishes. *Cyclohexanol* (Hexaline), $C_6H_{11}OH$, b.p. 160° C., f.p. 68° C., and 3-*methylcyclohexanol* (Heptaline), $CH_3 \cdot C_6H_{10}OH$, b.p. 170°-180° C., f.p. 60° C., may be used as special solvents instead of turpentine.³³ Hexaline is obtained by the catalytic reduction of phenol, which loses its phenolic properties through the introduction of hydrogen into the hydrocarbon ring. Heptaline is obtained by the reduction of cresol. It is stated that manila and kauri copals are easily dissolved by hexaline and heptaline, and are not precipitated on addition of linseed oil. Metallic salts of fatty and resin acids, likewise acetyl cellulose and rubber, are also soluble, but their most remarkable property is that of solubility in aqueous soap solutions and their power to absorb other solvents, e.g. benzol

and benzene, when in that condition.³⁴ Cyclohexanol and cyclohexanone are good solvents for Japanese lac.*

Fusel Oil.—The production and properties of propyl, isobutyl alcohol and *d*-amyl alcohol and isoamyl alcohol, the whole constituting the fusel oil from potato and grain spirit, are fully described in Monier-Williams' *Power Alcohol* and in H. Wolff's *Die Lösungsmittel der Fette, Öle, Wachse u. Harze*, and only those characteristics which are of interest to the varnish maker may be mentioned. Fusel oil boils between 90° and 132° C., according to its grade. As a solvent for transparent bleached lac it has the property of imparting good flow on the work, and owing to its slight affinity for water the lacquer films dry clear at the ordinary temperature, in contrast to the milky appearance when a more volatile hygroscopic alcohol is used. It must be pointed out that care must be taken in using the alcohol as a solvent, as the vapour, if in a concentrated form, has toxic properties. Its acetic ester, amyl acetate, is an excellent solvent for nitro-cellulose, and mixes freely with all oils and fats, and with organic solvents generally. It boils between 110° and 150° C., depending on its quality, and its vapour has no deleterious effects when proper precautions are taken.

Hexaline Acetate has been put forward as a substitute for amyl acetate; it is less volatile, and a better solvent.

Methyl and Ethyl Formates are of interest only as solvents for acetyl cellulose.

Acetone is an excellent solvent for oils and fats as well as of resins. It exercises a great softening action on a dried varnish film, and enters largely into the composition of varnish removers. Although fatty acids are soluble, the alkali salts of the solid acids (especially the potassium salts) are only with difficulty soluble. Fachini and Dorta³⁵ make use of this property to separate solid from liquid fatty acids.

Acetone Oil is the residue left in the rectification of acetone, and consists of ketones of variable composition. Methyl ethyl ketone, $\text{CH}_3\text{COCH}_2\text{CH}_3$, is contained in the colourless fraction (b.p. 70°-120° C.). The heavier oil (b.p. 120°-250° C.) is of a yellow colour and only slightly soluble in water. The high solvent power and slow evaporation render it useful in the varnish industry for special preparations, but it is apt to be variable in its behaviour, and its rather unpleasant odour does not make it popular. It would seem to bear the same relationship to acetone that fusel oil does to ethyl alcohol.

Physiological Action of Varnish Solvents.—In addition to the properties of the substances described in this section, it is most important to consider whether their vapours will have any deleterious action on the health of the workers. In a lecture delivered before the Royal Society of Arts (1921) on *Industrial Disease and Immunity*, Sir Kenneth Goadby stated that not only is the direct action of the vapour to be considered, but also secondary diseases non-specific to the industry which may be induced by the occupation. His investigations showed that the usual painters' colic, the acute attack of abdominal pain contracted by breathing the air of newly-

* Cyclohexanone, $\text{C}_6\text{H}_{10}\text{O}$, is a cyclic ketone and is an oxidation product of hexaline.

painted rooms, was due to turpentine poisoning, and is usually attributed to lead poisoning. Again, arterio-sclerosis resulting in increased blood pressure was a common disease among painters, although white-lead painters showed a lower blood pressure than those working with leadless paints. It would appear as if the vehicle which the painters use were a factor in the cause of the disease. C. T. Kingzett³⁶ contradicts the statement as regards turpentine for the following reasons: The Sanitas Co. in one particular part of their factory have a number of oxidisers containing thousands of gallons of turpentine constantly in action, so that the air is fairly fully charged with turpentine vapour, and yet during a period of more than forty years not one of the workers has been known to suffer from trouble of any kind, neither abdominal trouble, nor headache, nor suffering of any kind. This statement can be confirmed by the writer from his knowledge of the conditions of a varnish thinning shop.

One must distinguish between poisoning due to a high concentration of vapour under abnormal conditions and poisonous effects when small quantities of vapour are present in the air under ordinary circumstances. No one can deny that turpentine has a physiological action on the human system, but under ordinary conditions, with proper precautions as to ventilation and cleanliness on the part of the worker, there are no ill effects from its use. The action of turpentine, on the whole, is less harmful than the other solvents employed in the varnish industry. With reference to turpentine substitutes containing petroleum, good quality material is relatively harmless in a well-ventilated room. The presence of cyclic hydrocarbons increases the action of the petroleum, which acts essentially as a nerve poison, producing, when inhaled in strong concentration, paralysis of the limbs, headache, and unconsciousness. If by any chance an excess of vapour of turpentine or petroleum has produced such symptoms, then the first-aid treatment must be to bring the patient into the fresh air. In removing varnish from the hands fresh turpentine or a good neutral white spirit should be used, but the hands must be carefully dried, especially between the fingers, otherwise the skin is slowly destroyed and suppuration may ensue by continued contact of the spirit.

Benzol is a nerve poison like petroleum, but is three or four times as strong, and acts also on the blood;³⁷ whilst crude benzol is much stronger in its poisonous activity. The statement does not apply to vapours present in low concentration. Of the two ordinary solvents, turpentine and white spirit under proper conditions appear to have no ill effect on the workman. With benzol, and especially crude benzol, care must be taken.

In reference to the newer solvents, tetraline, dekalin and cyclohexanol, more experience is required, although they are stated to be quite harmless.³⁸

The chlorinated hydrocarbons are dangerous, especially trichlorethylene and tetrachlorethane. The vapour of tetrachlorethane acts on the liver with fatal results, and although it is a good solvent

for acetyl cellulose, its use has been forbidden. Reasonable care is required in handling chlorbenzol. Of the alcohols used in spirit varnishes, the vapour of methyl alcohol is dangerous and the use of wood naphtha requires very careful attention to the conditions of working. Amyl alcohol (fusel oil) may cause headache if the ventilation is inadequate. Acetone and ether require similar precautions. Carbon disulphide is especially dangerous, and its use should be avoided as much as possible. None of the substances mentioned above, with the exception of carbon disulphide, chlorinated hydrocarbons, and methyl alcohol, have serious effects on the system, provided proper precautions be taken for ventilation and cleanliness of working. Much more thorough investigation of the physiological action of industrial solvents is desirable. It is often difficult to draw conclusions from the results with animals; cf. the difference in action of hydrocyanic acid on a dog and on a man. Moreover, the action depends on the adaptability of the individual and on the normal state of health. It is of the highest importance that, before a new solvent be put on the market, a careful study be made of its physiological effects, because the success of its use depends not only on the quality of the solution produced, but also on the inactivity of its vapour on those who have to apply it.

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PART II

VARNISHES

CHAPTER XII

OIL VARNISHES

A VARNISH may be defined as a liquid which dries by exposure to air at the ordinary or at a higher temperature to a more or less hard transparent film, giving protective action or decorative effect to the surface to which it is applied. There are exceptions to the transparencies of varnishes, notably those known as Black Japans, their transparencies being apparent only in very thin layers.

Varnishes may be classified broadly into three varieties:

(1) Those which consist of a medium similar to that of paints (*e.g.* linseed oil, or other drying oils, and thinners), the hardness of which may or may not be increased by the addition of certain other substances miscible with or soluble in drying oil (*e.g.* gum-resins, rosin, pitches); such varnishes are classed as oil varnishes.

(2) Spirit varnishes, *i.e.* varnishes which consist of a solution of a resin in a volatile solvent or mixture of solvents with or without non-solvents.

(3) Varnishes consisting of the natural products of a tree, drying by oxidation assisted by enzyme action, *e.g.* Chinese, Japanese, and Burmese lacquers. In this class may be included certain oleoresins of the type of balsams, such as Canada balsam, or Venice turps, which are natural products capable of drying in the air to give hard transparent films.

Manufacture of Varnishes.—Oil varnishes represent the most important of the three classes referred to. For general purposes oil varnishes may be said to consist of four constituents, resin, drying oil, a volatile solvent, and an accelerator of oxidation (drier) of the drying oil and to a lesser degree of the resin. These products "dry" to a hard film mainly by oxidation of the drying oil in its semi-fluid union with the resin, assisted by evaporation of the volatile solvent. The application of a film or coat of varnish to a surface is done primarily with a view to affording protection against atmospheric weathering, wear and tear, etc. There are

exceptions, however, when the main object aimed at is to confer decorative effect by giving gloss or enhancing the beauty of the grain of wood. For either purpose certain of the constituents of oil varnish have the same effect. In the piano trade the high gloss finish is greatly prized, and French polishing has been largely replaced by varnishing, whereby after application of three coats of varnish, brushed or sprayed on, a highly polished surface is produced in a few minutes by rubbing over with a liquid supplied with the varnish. An American polishing oil consists of a non-drying mineral oil (motor oil), with a little pumice or rotten stone mixed in, which is rubbed on the varnished surface (thoroughly, dry) with a felt pad or a short bristle stub and a round pound brush.

As stated in a former chapter, linseed oil dries to a tough elastic film, but neither its hardness nor gloss is sufficient for satisfactory protective action or for desired decorative effect. The resin (the term comprising "recent" and "fossil" resins) is on the other hand a body devoid for all practical purposes of elasticity, but generally hard, fairly resistant to atmospheric effects and therefore stable, of high refractive index and hence conferring gloss.

Although the mixture or combination of oil and gum in a varnish does not possess the same high viscosity as it acquires after oxidation or drying, the unoxidised liquid is yet of such a viscous nature that it would be impossible of application without the addition of a diluent. This introduces the question of the volatile solvent. The solvents usually employed are turpentine or "white spirit," the latter representing a fraction of petroleum distillate having a flash point, mobility, and degree of evaporation more or less approaching those of turpentine. Other diluents are used as turpentine substitutes; shale naphtha, shale spirit, petrol, solvent naphtha, from coal tar, etc., but on account of their unpleasant smell, low flash point, or other objectionable features, they find limited application only for special purposes.

The question of the employment of genuine turpentine or its most popular substitute, "white spirit," has occupied the attention of varnish manufacturers to a considerable degree in recent years. On the whole, it must be considered that genuine turpentine is the most reliable solvent to obtain greater stability of a varnish mixing, to ensure easy application, satisfactory flow, and more reliable drying. Such an assertion is based on the fact of the smaller range of distillation temperature of turpentine (the petroleum distillate being a mixture of hydrocarbons of near boiling points), its more familiar odour, its good solvent power for resins and oils, which increases on exposure to air, and oxidation, and its very limited power of absorbing oxygen, which may stimulate to a certain degree the drying of the varnish film. In a previous chapter (p. 188) reasons have been put forward for the preference for turpentine over other solvents, and it is wise to emphasise them, as well as the fact of its more suitable viscosity and the slight solvent power on the undercoat, which some thinners possess to a high degree, whereby a sinking in of the coating is sometimes observed.

Coal-tar naphtha, known as "solvent naphtha" in the trade, has a greater solvent power for the usual components of a varnish than turpentine, but its unpleasant odour and toxicity are responsible for its general unpopularity as a turpentine substitute. It must be pointed out that turpentine confers no marked superior durability on the varnish film.

The remaining constituent of oil varnishes is the drier or accelerator of oxidation. The mechanism of the action of driers has been referred to in an earlier chapter, but it may be stated here that, of the metals known to possess catalytic action in accelerating oxidation, only the compounds of lead and manganese, and of late years, cobalt, have found general use. These driers are introduced either as oxides, carbonates, etc., or as the metallic salts of an oil or resin acid. In the former case the high temperature necessary for their solution results in a darkening of the finished product, so that the metallic "linoleates" or "resinates" find favour by reason of their solubility at low temperatures.*

From the foregoing it will be gathered that for all practical purposes the main constituents of the varnish film are the vegetable oil and resin. The simplest type of varnish would therefore consist of a solution of common rosin in linseed oil, with the addition of a suitable drier, reduced to a working consistency with turpentine. Such a preparation would indeed constitute a "varnish," and it is regrettable to state that it has in the past found a certain sale at the hands of unscrupulous dealers. Consideration of the nature of the non-volatile portion of such a preparation will show its poor properties and the results to be expected from its use in practice. In the first place the mere fact of the ready solubility of rosin in linseed oil is such that amalgamation of the two will take place at comparatively low temperatures, so that the linseed oil, having received no heat treatment to polymerise its glycerides to compounds resistant to atmospheric weathering, will on progressive oxidation show all the disadvantages of instability referred to in a former chapter. Moreover, the polymerisation of linseed oil is attended by an increase in refractive index, and the gloss resulting from or conferred by the oil constituent in the varnish will be a minimum. The other constituent, rosin, possesses certain properties, e.g. a tendency to slow crystallisation of the fused abietic acid and the production of a water-soluble variety, which render it unsuitable as a constituent of a varnish except under certain circumstances. Moreover, it is unstable to atmospheric effect, being prone to oxidation, especially in a thin film, and its oxidation causes a reduction in weight and in body, which latter effect results in a shrinkage of the surface apparent as cracking of the film. It has been stated that abietic acid gives peroxyacids capable of degradation, although resenes (stable inactive bodies) are formed at the same time. Paul (*loc. cit.*) has found water-soluble modifications of abietic acid produced from colophony, and also that some

* The solubility of the "resinates" increases with the resin acidity of the mixing.

of the oxidation products are soluble in water. The low melting point, low refractive index, lack of toughness and hardness, and a tendency to powder when rubbed up, contribute to the general unsuitability of ordinary rosin as a component of linseed oil varnishes except in comparatively small quantities.

In a general consideration of the product which long experience has shown to be composed of those ingredients which go to make a satisfactory varnish, viz. linseed oil and suitably treated fossil gums, it can be demonstrated how the necessary properties of the finished varnish are contributed by the ingredients. In view of the great diversity of properties of varnish components, it will be understood that many are apparently latent, and in some cases it would seem as if the specific properties were not worthy of consideration. However, in distinguishing high-grade products the small differences in the properties of the components become manifest, and the connection between composition and properties is clearer. A preliminary word is necessary on the subject of the fossil gum or resin. On examining a specimen of a fossil gum such as African Animi, Congo, copal or amber, its apparent suitability as a constituent of varnish is at once evident in so far as its brilliance and hardness are concerned. Thus it would seem that the ideal varnish might be obtained, if the hardness and lack of elasticity of one of these fossil resins were tempered by the influence of linoxyn from linseed oil.

Unfortunately there is no means whereby such a blending of properties of the two substances can be obtained, as the fossil gums (with the exception of kauri) appear to be quite insoluble in or immiscible with linseed oil. The high degree of polymerisation is considered to be the cause of their insolubility in linseed oil. However, depolymerisation of the gum, resulting in complete solubility in the oil under suitable conditions, is obtainable by a process of destructive distillation known among varnish makers as "running." In this treatment the depolymerisation is generally accompanied by a partial decomposition of the acids of the resins to yield anhydrides and resenes. The solubilised fused or "run" gum is, however, quite different from the gum in its native state, a considerable darkening in colour and a certain loss of hardness having occurred during the running process. The "run" product will have become soluble in linseed oil, whilst the hardness and high gloss conferred on the gum and oil combination will, under ordinary conditions of practice, bear a direct relationship to the properties existing in the natural product.

To understand the condition in which the several constituents exist, a brief account of the process of manufacture will be advisable. A description of the preparation of varnish on a laboratory scale will serve as an introduction to the large scale process.

The first part of the process consists in the fusion or running of the gum. Small pieces of gum, *e.g.* Congo, broken in pieces the size of peas, are sifted free from dust and introduced into a 250 c.c. silica beaker. The gum should not fill more than one quarter

the capacity of the beaker, on account of the great amount of frothing which occurs during the running. The beaker is heated over the free flame of a Bunsen burner, care being taken that the flame does not play above the height of the gum in the beaker.

(The first effect of the heat will be to sinter together the individual particles of the gum, the whole forming a treacly mass, whilst quantities of terpenoid vapours are evolved. As the heating continues, the fusion will extend to the slow heat-conducting particles of gum, until the treacly mass will have become converted into a viscous liquid. Considerable quantities of vapour are evolved, resulting in much frothing and a rise of the contents of the beaker, whilst the completely fused gum will begin to collect as a liquid darker in colour than the unfused gum. The heat is so regulated and vigorous stirring is continued that the maximum rapidity of complete fusion is obtained consistent with adequate control of the frothing. After heating for about thirty minutes, depending on the nature of the gum, the contents of the beaker will have become completely fluid. Although the temperature throughout the mass will be higher than at any previous stage in the operation, the head of froth will have considerably diminished. At this point the appearance of a sample withdrawn on a thin narrow metal spatula and allowed to fall back into the beaker would indicate to the practical gum runner the state of completeness of the fusion, as obviously large scale practice does not permit of inspection through the walls of the metal vessel used. At this stage the temperature will vary with the nature of the gum, the harder resin (Animi, Congo) requiring a higher temperature than softer resins such as Manila. The gum is now ready for the addition of the oil. At this point the evolution of vapours, which is considerable, is responsible for a loss of from 15 to 30 per cent of the weight of the gum taken, the degree of loss depending on the fossilisation (age) and the hardness of the gum. There appears to be a more or less constant figure for each class of resins representing the minimum loss in weight which must occur under factory conditions before complete solubility in the linseed oil is obtained, but it is doubtful whether this statement is strictly correct, and it will be criticised later. It has been proposed to check the progress of the operation by noting periodically the weight of the contents of the pot during fusion, but this is tedious and unreliable.

Under ordinary conditions of heating, too small a loss results in partial or even complete insolubility in oil, whilst excessive loss results in reduction of hardness and darkening of colour of the finished product. The fused gum is, however, not so soluble in oil, as is the case with many other products possessing the same range of solubility in different concentration; thus, if it be desired to make a varnish composed of equal weights of gum and oil, the addition of the whole of the oil at once would induce a chilling of the gum with a consequent lowering of temperature, and would cause its immediate precipitation. In practice the oil is added hot, in small portions, until a test spotted on glass shows a milky

appearance on cooling, indicating that the union of the gum and the oil is becoming incomplete. The temperature is then raised until a test sample shows by its clearness on cooling that complete union of the two has been brought about, when a further addition is made until the whole of the oil required has been introduced. The remainder of the treatment necessary to convert the mixing into a finished varnish is the addition of a suitable volatile diluent to render the product easy of application. The acceleration of its drying powers is brought about by the introduction of a drier.

The viscous resin-oil substance is removed from the source of heat and allowed to cool to a temperature approaching that of the boiling point of the solvent chosen, 160°-170° C. in the case of American turpentine. Addition of thinner is then made, care being taken that thorough stirring is maintained during the addition so as not to chill locally particles of the product. The quantity required will depend not only on the viscosity desired for the finished product, but on the consistency of the varnish before addition of the thinner. The acceleration of drying properties in the product is obtained, as already stated, by the addition of a compound of one or more of those metals which are used to promote drying properties in oils, such as lead, manganese, cobalt, etc. The catalyst may be in the form of an organic compound of the metal soluble in the finished varnish, *e.g.* lead, manganese or cobalt linoleates, or rosinate, and may be introduced either after the addition of the thinner or by causing union of the metallic base of the catalyst chosen with the gum and oil at an elevated temperature (200°-300° C.) before the addition of the thinner. In the latter case the base combines partly with any free fatty acid or resin acid present, and if in sufficiently large quantity may partially saponify the neutral glyceride of the oil.

Running of Gum.—The manufacture of oil varnishes on the factory scale differs in no material respect from the laboratory procedure described above. The fusion or "running" of the gum (see Fig. 25) may be performed in copper, aluminium, or ferro-nickel vessels of various shapes and capacities (30-100 gallons). In some cases the pots have a sheet-iron body with copper bottom. The dimensions of an English running pot for a charge of 60 lb. of gum are 3 ft. high, 2 ft. upper diameter, 1½ ft. lower diameter. In England the charge of gum per pot may be as much as 112 lb. or more, with corresponding modifications of the dimensions (Figs. 25A, 25B, and 25C). In America the gum running pot for a 125 lb. charge is 3 ft. high and 3 ft. diameter. In France the pots are much smaller, and often contain only a 6 kilos. charge of gum.

Harrison¹ has investigated the effect of the metal from which varnish kettles are made on the colour of the products. The experiments were on the laboratory scale only with iron, copper, aluminium, and copper-aluminium alloy pots. Each pot was used in the preparation of heat-bleached linseed oil, bodied oils, rosin-tung-linseed oil, and Congo-linseed oil varnishes. The products were graded in colour to Lovibond tintometer inspection. (In

general the varnishes prepared in aluminium kettles were the palest, those in aluminium-copper alloy pots were next in order, followed by those in copper, and the darkest were from the iron receptacles, but the results were not strictly uniform. It is stated that a copper-aluminium alloy vessel corrodes less than a copper vessel on heating. With large aluminium pots the heavy walls prevent rapid cooling of the mixing, and large holes are frequently burnt through the bottoms of the kettles, due to the settling of the dirt which causes local overheating. The discoloration of the varnish



FIG. 25. Gum melting pot (English), with cover.

products is probably not due entirely to the solution of the metal, but partly to its catalytic action on the oxygen absorption of the oils:

The statement that the polymerisation of tung oil is retarded in aluminium pots cannot be accepted as correct. Experiments with pots of silica, aluminium-coated iron, and iron-silicon alloy have been suggested. It is doubtful whether the results given above would be confirmed on a factory scale of operations. For durability copper or copper-iron pots are generally superior, and as to colour, this is more likely to be governed by the fact mentioned above than by the nature of the metal used, provided the temperature is not too high. However, it must be admitted that aluminium pots give a paler varnish than copper or copper-iron, but the life

of the aluminium pot is shorter. Copper-bottomed pots with an aluminium upper part ought to provide suitable durability. In France, tinning has been tried without success, also nickel-plating, but this is expensive and does not last well.

The hearth on which the running is carried out consists usually of a hole in the floor of the "making house," beneath which there is a grate with a flue running underground, constructed so that an intense bright fire may be obtained and the products of combustion can be withdrawn completely. With reference to the fire-pit, standardisation of dimensions is desirable for rapid replacement of the pot and the fire hearth.

In many text-books on varnish technology, elaborate drawings are given showing details of running hearths and pots or representations of gum melting rooms

(Salin, *Technology of Varnishes*; "Melting Room of the Murphy Varnish Co. at Chicago"; Seligmann and Zieck: "Moderne Schmelzanlage von H. C. Sommer in

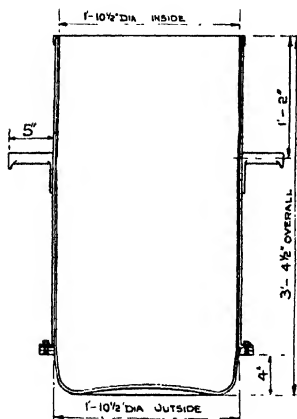


FIG. 25A.—Section of gum melting pot.

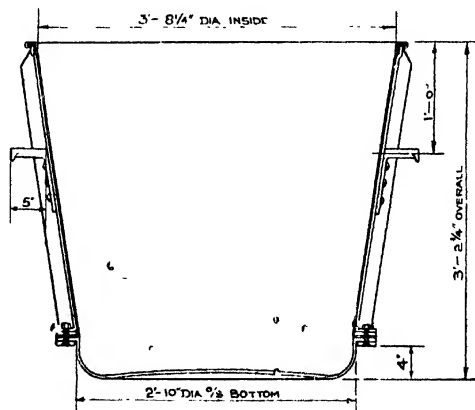


FIG. 25B.—Section of gum melting pot.

Düsseldorf"; Coffignier, *Fabrication des vernis gras*: "Ouvrier cuisant les gommes"). The hearth may be fed either from the outside or from inside the running shop, and the fuel may be either

coke or gas using special burners, or oil, as in boiler installations where oil and steam replace the solid fuel. It must be pointed out that the control of temperature during the heating is of importance; too long fusion means loss of colour and hardness of the gum, insufficient sweating entails incomplete solution of the drying oil. Too fierce heating tends to unequal depolymerisation, so that part of the gum is "overrun" and part "underrun." It is for this reason that coke fires retained their popularity so long, as they were easily controlled by the skilled runner and generally cost less than gas fires. Nevertheless, the convenience of gas and oil fuels makes their use very attractive, provided the regulation of temperature is satisfactory. During the running process the contents of the pot are stirred vigorously by a special

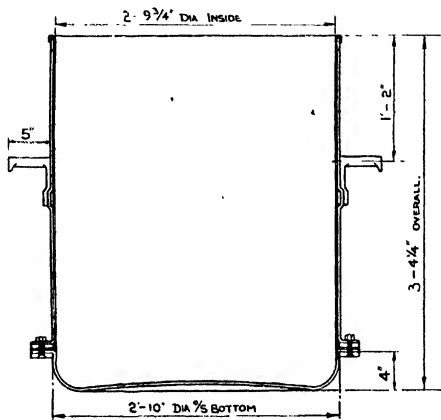


FIG. 25C.—Section of gum melting pot.

form of stirrer, and the condition of the gum is examined periodically by withdrawing a portion by the stirrer and allowing the gum to fall back again into the pot. A form of hood is shown in Fig. 25; in principle it consists of a hood hinged suitably on to the fume flue-pipe and provided with a covered window for the introduction of the oil and a partially covered opening for the manipulation of the special hand stirrer. The making house itself consists of a cement-floored shed, well illuminated and furnished with as high a roof as possible in order to provide for the contingency of accidental ignition of the contents of the pot. The fumes given off during the running process pass either to a fan or chimney shaft or alternately to a removable cover fitted with a delivery pipe leading to a fan and suitable condenser installation. The recovery of the fumes will be dealt with after the detailed description of the gum running. In practice the operation of gum running is usually carried out by two workmen, the

gum runner and his assistant. A suitable quantity of gum, usually 112 lb. or more in modern practice, is weighed into a clean pot and the latter brought to the fire in the making house on a trolley or truck, occasional stirring being resorted to during the first or sintering stage of the fusion; as liquefaction of that portion of the gum immediately in contact with the bottom of the pot proceeds, close observation has to be made in order to guard against the danger of a sudden frothing of its contents. As the gum approaches complete fusion, vigorous stirring is resorted to, until finally the gum runner judges the "run" accomplished by observing on the stirrer the fluidity of the melt. The time taken for a charge to be run depends on a number of factors: (1) the nature of the gum; (2) the amount of the charge; (3) the mode of heating; (4) the nature of the metal of the pot. Generally half an hour to an hour may be taken as the usual time.

The behaviour of the gum during the sweating has been adequately described in the laboratory experiment. The requisite quantity of oil is added either by the assistant cautiously pouring warm oil from a vessel known as a "jack," not unlike a watering-can with an old-fashioned kettle spout, or in more modern practice the previously heated oil is pumped into an overhead tank fitted with a graduated gauge glass marked off in warm gallons, from which it is allowed to descend in a thin stream into the gum pot, the contents being in the meantime vigorously stirred. The oil must be added in portions at a temperature of not less than 300° F. After each addition the runner withdraws on his stirring rod a few drops of the mixing on to a glass plate. If the sample cools to a clear film, it shows that incorporation is satisfactory and more oil may be added; if cloudy, the mixing must be heated until a sample is bright when cold on the glass trial plate. The amount of oil to be added will depend on the varnish required. The addition of thickened linseed oil is generally made last, and the mixing finally heated until the head begins to rise, when it is quickly transferred to the adjoining shop to be cooled. It is quite easy to incorporate run gum in thickened linseed oil with satisfactory results, and under special circumstances run gum can be incorporated with heated tung-oil to give stable mixings.

Introduction of Driers.—The rules governing the addition of the driers to linseed oil apply equally in the case of a varnish, so that the varnish maker has at his disposal the choice of several metallic compounds having different degrees of solubility, etc., in order to produce the effects he aims at in the finished product.

To recapitulate, the common metals used as driers may be summarised as follows: Class 1, lead, iron; Class 2, manganese, cobalt. Lead and manganese may be added in the form of oxides; cobalt, manganese, and lead may be conveniently added in soluble form as resinate, linolate, or tungate. The use of iron as a drier is restricted considerably by the dark colour of its compounds, but when introduced it is usually added as umber (iron and manganese oxides) or Prussian blue. Iron may also be introduced in the form

of a linoleate obtained by treatment of linseed oil acids with iron filings (*vide* Oil Acids, Chapter V. page 91).

A distinguishing characteristic of lead dissolved in linseed oil is its property of forming an insoluble salt (lead stearate, palmitate, and possibly some oleate), which becomes apparent as a cloudiness when the varnish is cooled and subsequently settles out as a precipitate after a period of weeks or months, leaving the varnish bright.

Lead resinate has less tendency to be precipitated or to produce a turbidity, but it is not very soluble, and when in excess the settlement of the "foot" is usually fairly rapid. The large proportion of lead resinate which is necessary, by reason of its comparatively low concentration in lead, militates against its use by reputable varnish makers; this applies in general to all resins except cobalt and manganese (*vide* footnote on page 199).

Manganese and cobalt have very similar properties in their effect on varnishes, in so far that they have a tendency, when present in excess, to cause surface-drying or "rivelling," instead of producing a drying effect throughout the thickness of the film (see under Defects of Varnishes). Both these metals require only a small proportion to accelerate considerably the drying of the varnish. The combination of lead-cobalt or lead-manganese is usually resorted to, excepting where the presence of the former metal is undesirable. The use of lead alone in a varnish is uncommon, owing to its relatively slow drying powers.

In addition to the method of adding driers to the gum-oil combination, yet another method has found a certain amount of favour with some manufacturers; this consists in the addition of insoluble driers to the finished (thinned) varnish, solution being effected by long agitation in large drums. This method, known as "drumming" or "churning," has the advantage of yielding considerably paler products; probably by reason of the tendency to darkening of the metallic soaps forming the drier at the somewhat elevated temperatures of solution necessary in the method described above. The agitation with air in the drum, to which the varnish is subjected, also induces a certain amount of bleaching action. Drummed varnishes have also the advantage of a lesser tendency to skin-over when stored in bulk in open tanks, but they require longer periods for clearing than varnishes in which the drier has been dissolved at a high temperature.

After the introduction of the drier, the varnish pot is removed from the fire and taken to a cooling room, where addition of the thinner is made after the contents have been cooled down to a temperature of 160°-170° C. In some cases the solution of the drier may be added to the thinned gum-oil mixing. This operation requires little description, the turpentine or substitute chosen being added slowly with continual agitation of the mixing. Addition of the thinner at too low a temperature may cause precipitation of the resin in certain cases, whilst addition at too high a temperature will occasion losses owing to volatilisation. Moreover, delay in adding thinner may also result in incomplete solution, especially

in the case of varnishes containing a high percentage of resin. It would appear as if the colloid mixing were stable only within comparatively narrow limits of dispersion and temperature. The necessary conditions are a matter of experience. The varnishes are thinned to a required viscosity, which may be determined by the "bottle" method standardised against a determination by an Ostwald or Doolittle Viscometer.

Other Processes for Running Copals.—Mention has been made of processes to depolymerise gums under pressure without loss.² The principle is solubilisation in the presence of naphthalene under pressure (4 atm.) at 275° C. in an autoclave fitted with a stirrer. At the end of two hours the change is complete, part of the necessary oil is added, and heating is continued for one hour at 280° C., followed by the removal of the naphthalene by distillation under reduced pressure. Coffignier states that an autoclave on the Terrisse plan worked satisfactorily for five years (1906-10) with a charge of 150 kilos. of gum at each operation. The advantages claimed are: (1) Utilisation of the whole of the copal; (2) paler varnishes are produced; (3) the original hardness of the resin is retained. In a later patent by Terrisse and Coffignier, copal oil and copal are heated with naphthalene under pressure. If the resin, solubilised by copal oil, be esterified with an alcohol, *e.g.* glycerine or benzyl-alcohol, there is an increase in weight of the resin.³ In the recent specifications the copal solubilised, either by ordinary sweating, by naphthalene, or by naphthalene with copal oil, is heated with glycerol or benzyl-alcohol to transform it into an ester. The Terrisse process is an improvement on that of Graham and Burrell,⁴ in which the copal was heated to 350° C. under pressure with turpentine. The colour of the varnishes by Burrell's process are not good, whereas those obtained by Terrisse's process are satisfactory and the varnishes are of good hardness. The objections to the autoclave processes are the capital outlay and the length of time of the running process, which tend to outweigh the loss of the resin treated in the ordinary manner. Recently the difficulties arising from the loss of weight of the gum have been shown not to be serious, for it is possible to utilise the crude copal oil in the manufacture of varnishes of satisfactory quality without having to go to the expense of setting up new plant. Other special solvents for copals have been proposed, *e.g.* linseed oil acids, amyl alcohol, terpineol, etc., but they have met with no success. The effect of the solvent materials on the finished product is deleterious, unless they can be completely removed, which is not feasible.

COMPARISON OF THE PROPERTIES OF RAW, RUN, AND SOLUBILISED RESINS (Coffignier).

	Madagascar.	Madagascar "run."	Madagascar solubillised by Naphthalene.
Specific gravity at 16° C. . .	1.058	1.062	1.061
Melting point	> 300	205	165
Acid value	93	68.2	68
Köttsdorfer value	70	45	66
Percentage of Insolubility :			
Alcohol	74	92	74
Ether	65	52	20
Turpentine	60	3.6	52
Benzol	78	1.5	40
Chloroform	69	1.7	sol.
Carbon tetrachloride	85	4	26

Maturing of Varnishes.—The varnish prepared as indicated above does not possess properties which the manufacturer would consider requisite for a satisfactory product. The varnish will hold in suspension fragments of gum bark, mineral matter, etc. Moreover, a heavy cloudiness may develop a few hours after the varnish is cold, due to the action of the driers. In general the turbidity originates from the same cause as that accruing from ordinary boiled linseed oil prepared with a lead drier, and is caused by the precipitation of the insoluble lead soap of the saturated fatty acid component of the oil, *e.g.* stearic, palmitic, and myristic acids.* On tankage the debris from the gum and the lead "foot" will settle out, leaving a clear varnish. Simultaneously with the deposition of the "foot," other changes occur, *e.g.* a slight bleaching of the varnish. A varnish of a decided brown colour immediately after manufacture will become a yellow orange after a year's tanking, especially if manganese driers be present.

Certain undefined physical changes, probably connected with alteration in the arrangement of the disperse phase in the colloid solution, will also occur on "ageing," viz. an improvement in flow under the brush. It must be remembered that in the running of gum the strong depolymerisation necessary to render it soluble is not a stable stage, and maturing will indicate a partial re-polymerisation; moreover metallic soaps of the driers present in the mixing will undergo a gradual increase in viscosity.* Lead oxide or lead linolate dissolved in linseed oil becomes stouter in consistency on storage, even when out of contact with the air. That such changes can be observed and identified with changes of viscosity has been mentioned in a paper by Seton, Probeck, and Sawyer.⁵ It is certain that the more reputable varnish manufacturers require a period of maturity by "tanking" for a period

* If a lead salt of a resin acid be used, unless the resin acidity of the mixing is high there will be a gradual deposition of a lead resinates.

of six months to two years. It is essential to maintain this old custom to a certain degree, as storage is necessary apart from what is required to produce complete clarification. No doubt the period may be shortened in many cases by filtration from the sand and gum dirt, but the removal of the lead "foots" is difficult, unless they are present in small quantities, otherwise it is best to draw off the clear varnish from the tank and treat the "bottoms" separately.

Filtration of Varnishes.—The removal of suspended matter in a varnish is always difficult, because of its viscosity. The warming of the mixing will cause a decided reduction in the viscosity, but this is not to be recommended, owing to loss of thinners and subsequent thickening due to surface oxidation and to partial solution of the suspended matter. In text-books many methods of filtration are described, but reference will be made here only to two classes of processes, (1) plate filtration and (2) centrifugal treatment.

The filtration of varnishes must be considered from the standpoint of the principle of technical filtration. The fundamental point to be noted is that for a given system of solid and liquid the whole problem is completely determined physically. The limit to the filtration is an economical one only: it depends on the way in which higher pressure increases the first cost of the plant, and, the pressure being given, on the balance between the cost of obtaining a thicker "cake" and the cost of removing it at more frequent intervals. The proper adjustment of these factors presents no difficulty to any one in designing filtering apparatus.⁶ It is evident that the above statement does not strictly apply to the varnish manufacturer. He deals with fluids of high viscosities, containing small amounts of suspended matter partly coarse, partly fine, and partly slimy, the latter being exceedingly undesirable for removal by filtration. The coarse material may be eliminated by straining through muslin, a preliminary and primitive method. It is not advisable to refer to old-fashioned methods, and the attention of the reader will be called only to the use of filter presses and centrifugal separators.

Filter Presses.—A summary of the construction and meaning of the numerous variations of the type of filter presses will be found in a paper by E. A. Alliot.⁷

Construction of the Filter Press.—A filter press may be described as a frame in which a number of loose slabs of filter surface may be clamped to form a series of hollow chambers capable of withstanding internal pressure. The filter surface is ribbed or grooved and covered with cloth and filter paper. This arrangement gives a maximum of area in a minimum of space, and is capable of modification to meet the varying conditions called for by different grades of material. A large variety of constructional materials can be used, and the whole plant is of high reliability and free from any tendency to break down.

The two forms of press in general use are (1) the recessed plate type, and (2) the flush and distance frame type, often called the chamber and frame presses respectively. The latter type alone is

used in varnishes, where only slight suspensions are dealt with. In the flush plate type the faced joint surfaces are practically flush with the filtering surfaces, the chambers being formed by frames having faced surfaces corresponding to those of the plates, and placed alternately with the plates. The cloths or layers of filter paper and cloth are hung over the plates so that each chamber has a cloth on both sides. The inlet of the material is through a passage having ports communicating to the interior of the distance frames. The liquor enters the chamber under pressure, the solid portions being retained by the cloth, whilst the fluid passes through and is drawn along the grooves or corrugations of the plates to the exit ports. For varnish filtration the presses are sometimes made with three or four passages situated at the corners of the chambers; one of the lower passages serves as a feed inlet, while the others

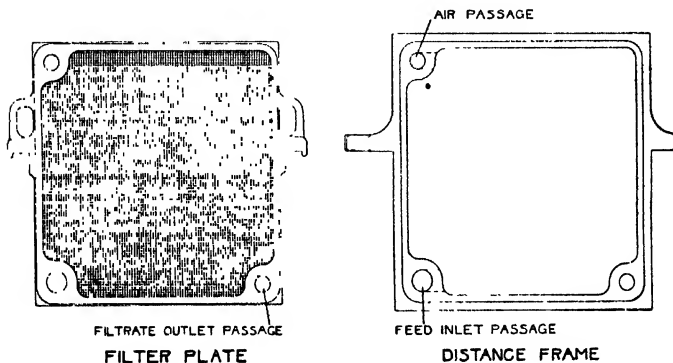


FIG. 26.—Plate and frame of Johnson filter press.

act as filtrate outlets, being joined together at the head of the press. By this arrangement the liquor has a minimum distance to travel along the grooved surface to get to the outlet passage. Further the upper passages ensure a free escape of the air from the chamber (see Fig. 26).

The press plates are usually made of iron with fine straight grooves or coarse pyramids or lozenge-shaped protuberances on the surface, so that the channels are kept sufficiently deep and narrow and cannot be closed by the sag of the cloth. To fix the filter cloth in the press a strip, long enough to cover both sides of the plate, with holes cut in it corresponding to the feed passages, is hung over the top of the plate. The question of the best material for a filter cloth depends largely on the liquid to be filtered. A strong, comparatively coarse cloth may be used to support a thin lightly woven twill or a good quality filter paper. With varnishes the deposit is so slimy, that an impenetrable layer is speedily formed on the cloth, so that it becomes almost impervious. Addition of calcined

fullers' earth, or diatomite, tends to build up an open structure in the slime and permits a more rapid flow. The best success of a

filter press installation depends not only on the choice of plant, but more especially on those in charge of the operation. It is nearly always possible to reduce high labour and cloth charges by proper methods in the lay-out of plant, and those who take these facts duly to heart will obtain the most satisfactory results. There seems little doubt that filtration of varnish through such a press yields the best clarity, although it is often advisable to remove most of the suspended matter by a previous treatment in a

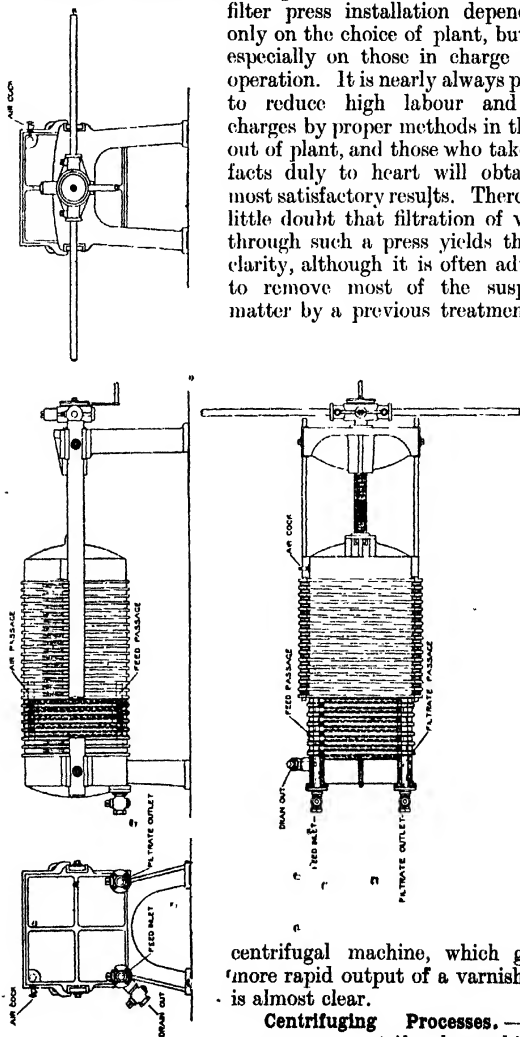


FIG. 27.—Johnson varnish filter press.

centrifugal machine, which gives a more rapid output of a varnish which is almost clear.

Centrifuging Processes.— There are many centrifugal machines on the market, but one especially suited for the filtration of varnishes is the modification known as the Sharples supercentrifuge (Figs. 28

and 29).⁸ The separated solid is deposited on the inside wall of the tube or bowl and is intermittently removed when the bowl becomes too much charged with solid (a bowl will hold about 15 lb. of solid before it requires removal). In the Sharples machine a separating force is developed 16,950 times that of gravity, corresponding to 17,000 r.p.m., although in the laboratory form a force of 40,000 times that of gravity can be developed. Since centrifugal force varies directly with increase in diameter and as the square of the speed of revolution, the centrifuge is of tubular pattern. The rotating bowl is both supported and driven from the top, being otherwise free to find its own axis. By this means the machine is operated with the minimum wear and tear. One main ball bearing constitutes the sole point in the machine at which friction has to be taken into account. The drive arranged immediately above the main bearing may be :

- (1) A belt drive from a line shaft.
- (2) Direct steam drive by means of a turbine wheel fixed to the tube or bowl spindle.
- (3) Indirect electric drive, i.e. an individual motor mounted on the centrifuge body and driven by a short belt and idler pulley on to the head of the bowl spindle.
- (4) Direct electric drive in which the motor armature is mounted on and is an integral part of the bowl spindle. Mechanical friction losses are thus limited solely to those of the one ball bearing which carries the rotating bowl, whereby a considerable reduction in the consumption of power is effected.

At the bottom of the bowl a short extension runs with a definite permitted clearance in a bushed socket, serving as a guide during the running up to speed of the bowl, when slight vibration or oscillation may occur. The liquid to be treated is admitted through the hollow centre of the extension of the bowl, under greater or less head, according as viscosity or other considerations demand. In dealing with varnishes it is sometimes advisable to warm them to about 120° F., in order to reduce the viscosity and to increase the flow. Settlement takes place during the upward travel of the liquid which discharges at the top of the machine. The suspended solids are deposited on the inside wall of the tube, and are intermittently removed from the bowl when it becomes fully charged. The Sharples supercentrifuge has had considerable success in dealing with nitrocellulose varnishes.

The Sharples machine can treat 100-150 gallons per hour, depending on the viscosity of the varnish.

In practice, clarification with the centrifuge is not profitable when the liquid contains more than 1-2 per cent of solids. In such cases other forms have to be used.*

* The Sharples clarifier removes "gum dirt," but to obtain a perfectly clean varnish film on a panel a period of tanking is advisable or final clarification can be obtained by passing the varnish through a filter press. It must be pointed out that the machine will not effect the removal of "bottoms" the solubility of which is affected by temperature.

The de Laval separators, which have been tried by a number of American varnish firms, consist of a multiple clarifier bowl or

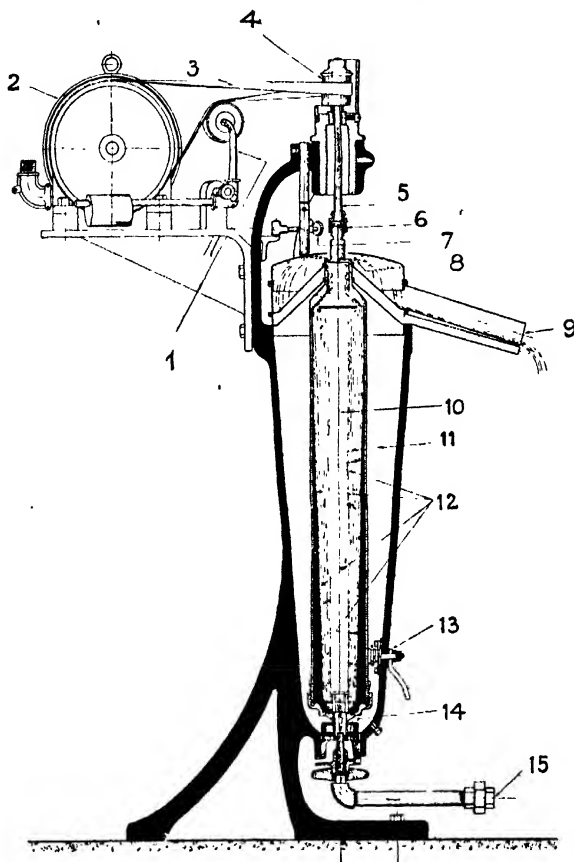
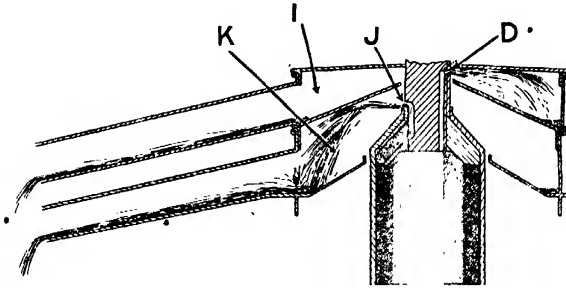


FIG. 28.—Sharples varnish clarifier.

- | | |
|---|---|
| 1. Idler arm and pulley for keeping constant tension in belt. | 9. Clarified varnish outlet. |
| 2. Motor. | 10. Bowl or rotor (17,000 r.p.m.). |
| 3. Belt. | 11. Vrnish under centrifugal force. |
| 4. Belt head bearing. | 12. Foots, etc., separated from crude varnish. |
| 5. Bowl spindle. | 13. Brake for bringing bowl to rest. |
| 6. Spindle to bowl coupling nut. | 14. Guide bushing for bowl bottom to revolve in. |
| 7. Speed indicator. | 15. Crude varnish supply by pump or gravity feed. |
| 8. Clarified varnish discharging from outlet ports in bowl. | |

a centrifugal filter bowl containing two chambers, an outer, where partial clarification ensues, and an inner, provided with plates

between which filter paper is placed. The bowl is a plain cylindrical



Morrell's "Varnishes," To face page 214.

ERRATUM

Page 215, line 1, "The bowl," to page 216, line 4, "fifteen minutes." This passage applies to the Sharples, not to the de Laval, machine.

The following describes the working of the de Laval Separator: The product to be filtered passes into the top of the bowl and flows to the bottom, where it is forced to the outer, or clarifying, chamber. Here the heavier and more easily removed particles are forced against the outer wall of the chamber. The partly clarified fluid passes to the inner chamber, where it enters the openings in the several plates, percolating under slight vertical pressure through filter paper and thence inward and upward to the discharge outlet.

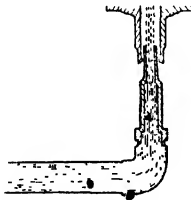


FIG. 29.—Sharples oil separator.

tube closed at its upper end, with a head provided with outlet ports. It is equipped with a removable set of wings which serve

to keep all the parts of the liquid at the same speed of revolution as the bowl. The bowl bottom containing the inlet port may be readily removed and the whole cleaned and replaced in about fifteen minutes.

Another form of filter suggested is the Sweetland filter for the clarification of liquors containing solids which do not filter freely. In this machine the solid is dislodged from the filter surface by means of a stirring mechanism without opening the filter, thus giving at all times a clean filter surface.

The separator type of Sharples supercentrifuge is for the separation of mixtures or emulsions of immiscible liquids, the liquids being continuously and separately discharged. Figs. 28 and 29 show the difference between the process of centrifugal clarification and separation. In the separator the heavier liquid forms a uniform cylindrical column against the shell of the bowl, and the lighter liquid an inner cylindrical column.

The Storage of Varnishes.—The varnishes are pumped from the thinning room, after a preliminary straining to remove gum dirt, into large rectangular or cylindrical tanks of galvanised iron with sloping bottoms of a capacity up to two or three thousand gallons. The height of the tanks is generally two or three up to five times their width or even more. The temperature of the storage room is maintained at 15°-18° C., and the rooms are warmed by hot water pipes. Clarification proceeds from the surface downwards, and the rate depends on the varnish and on its viscosity. The clear varnish is drawn off through special taps placed in the tank, the lowest being some distance from the bottom. A tap in the base of the tank will allow of complete emptying, so that the sediment may be withdrawn. From time to time the empty tanks are "seabbed" to remove varnish skin. Loose iron covers on the tanks protect the contents from dust. Periodically samples are withdrawn and tried on prepared boards, or on glass, for clarity, quality of surface, and time of drying. Any alteration in the viscosity is also observed.*

The Properties of Varnishes on Application.—In considering the uses to which oil varnishes are put, the main field of application is that of the protection of metal and woodwork. Besides their use as protective coatings, they have also an important function in the beautifying and accentuating of the natural grains of wood or conferring a high lustre or polish to the surface. The accentuation of the natural grain of the wood is accounted for by the penetration of the surface films by the varnish, thus producing optical continuity with a resultant exaggeration of the darkness of the grain.

From a protective standpoint varnishes must be chemically stable to atmospheric influences (oxidation), physically stable to changes of temperature (elastic), waterproof, and sufficiently hard to

* During the tanking of varnishes a slow shrinkage in volume occurs, due chiefly to evaporation of the volatile solvent and to slow oxidation of the turpentine. The rate depends on the "thinner" and on the conditions of storage. The loss of volatile thinner may vary between 2 and 7 per cent.

resist wear. It will be readily granted that, in view of the extreme tenuity of the average coat of varnish (about 1/750 in.), more than one coating will be necessary to give the desired result; and further, it will be apparent that the necessary properties must be considered which each coating must possess to fulfil its desired function. In the first place a preliminary coating will be necessary to stop the capillarity of the surface cells of the wood and at the same time "set" these cells to a hard rigid layer to obtain a solid foundation. Such effect is obtained by the use of a varnish of fairly low viscosity to ensure penetration of the cells of the wood, but having its gum and oil constituent of rather high viscosity so that such penetration, once secured, will not go on indefinitely, since a surface sealing is the only object aimed at. Rapidity of drying will also increase the surface sealing. Such an effect is obtained by the use of a varnish known as "goldsize": this product is a varnish in which the gum and oil combination has been brought to a viscosity approaching solidity, a liberal addition of volatile solvent ensuring a low viscosity of the finished product. The nature and amount of the driers added cause rapidity of drying. Such a varnish is of limited utility, possessing little gloss of film (owing to the large bulk of thinners present), low weather resistance, and slight impermeability, but it fulfils the purpose for which it is intended. It may also be incorporated with oil colour to give a hard bound undercoat on which subsequent coats of varnish may be laid. A solution of shellac in methylated spirit will also perform the same function.

Previous to applying a priming coat of paint or filler on wood containing knots, it is necessary that the latter should be treated with a liquid known as "knotting." If this were not done, the resin exuding from the knots would penetrate the paint and discolour it. A favourite stopping for woodwork is a mixture of dry whiting and dry white lead, made into a putty with linseed oil, to which 10 per cent of boiled oil has been added. Turpentine may be used as a thinner, and two coats of the stopping are brushed on with a stiff bristle brush and the surface rubbed down with pumice and water or with sand-paper. Priming coats may take other forms, *e.g.* fillers of silica or silicates incorporated with turpentine or a drying oil capable of giving a hard coat. An English filler may consist of carbonate of lime 50 parts, clay 46 parts, and graphite 4 parts; a German filler may consist of carbonate of lime 55 parts, clay 60 parts, and graphite 5 parts; an American filler may contain a silicate of alumina and iron containing 57 per cent silica, 21 per cent alumina, and 9 per cent oxide of iron. The filler is worked up with white lead and ochre in linseed oil, to which are added turpentine, an oil varnish, and liquid driers. The stiff paste is applied to the wood and the coating rubbed down with glass paper after twelve hours. Other varieties of wood filler may consist of (1) sifted kaolin 34 parts, boiled linseed oil 11 parts, gum driers 5 lb., turpentine 15 parts, and rosin varnish 154 parts; (2) emery 25 lb., linseed oil 15 lb., pale gum driers 1½ galls., rosin

varnish 17 galls., and white spirit 3½ galls. An American paste wood filler consists of a mixture of starch or dextrine, a mineral substance, and a linseed oil varnish made quick-drying by the addition of driers. The mixture is applied as a varnish, and after twenty-four hours should be dry enough to be rubbed down with glass paper.⁹

Transparent wood filler for aircraft propellers consists of a material in the form of a stiff paste requiring an addition of turpentine or white spirit before use. When the filler is applied to woodwork the grain of the wood must become filled in a satisfactory manner. The filler consists of filling material, at least 50 per cent of which must be powdered quartz, genuine linseed oil, and a good quality flattening varnish or gold size, in such proportions as to produce a preparation satisfying the requirements of the clauses of Specification 2 X. 11, 1920, British Standard Specification for Aircraft Material. The paste, suitably thinned with turpentine, when applied to a hard wood, such as walnut or mahogany, shall give a film drying sufficiently in half an hour at 70° F., so as to allow the excess to be "wiped off." When the paste, suitably thinned with turpentine or white spirit, is applied to wood, the film produced after fifteen hours' drying at 70° F. shall withstand sand-papering without rolling or clogging the sand-paper. When the filler (suitably thinned as above) is applied to a glass plate, the film produced after twenty-four hours' drying at 70° F. shall not become softened when immersed for four hours in distilled water at the ordinary temperature.

The specification for a priming varnish (2 X. 14, 1920, British Standard Specification for Aircraft Material) requires that the varnish may be either gold size or a spirit varnish, providing it is a satisfactory wood filler. The varnish when "flowed on" a glass plate shall become dust dry at 70° F. in not more than five hours. The film when allowed to dry for forty-eight hours at 70° F. on glass shall be bright and clear, and shall not roll up or powder when rubbed with the finger.

To fill up inequalities on the surface of iron, equal parts of red lead and gilders' whiting are mixed with 2 parts of genuine linseed oil and 1 part of gold size to a putty-like consistency. It must be used fresh, because it soon dries hard. A very effective primer for wood may be made from casein, dissolved in sal ammoniac solution. The mixture may be applied with brush or with spray, and will give a smooth, uniform surface on which coats of paint may be applied to good advantage. The primer may be coloured to suit the conditions.

In the preparation of the surface in carriage varnishing it was customary to apply two priming coats of white lead or oil followed by five coats of a mineral filler, a guide coat of bright red oxide stiffened with black japan, another coat of priming, a coat of vegetable black ground in oil and thinned with gold size and turps, finally two coats of oil colour thinned with gold size and turps, i.e. twelve coats before the varnish was applied.

Having now formed a preliminary base or groundwork, the succeeding coats which go to form the protective film may be considered. From an examination of the properties of the constituents of an oil varnish and of the effect which it is desired to produce, it is evident that from a decorative point of view it is desirable to obtain as high a finished gloss as possible, and to that end the relatively high refractive index of the gum resins is an important factor.

For the "bodying-up" or "undercoats" a varnish rich in resin is desirable. The relative hardness of such short-oil varnishes is of advantage from the standpoint of rapidity of drying and of solidity. Experience has shown that for the application of succeeding coats of varnish, the glossy coat of the preceding layer does not form a satisfactory "key" to the next, and it is necessary to prepare the varnished surface so as to give "tooth" or "bite" by removing the gloss from the surface. This is performed in the operation known as "flatting," which consists either in lightly sand-papering or in rubbing down the thoroughly hard and dry surface with powdered pumice stone and water applied with a piece of hard felt. Steel wool may also be used for rubbing down.

Such a prepared surface is devoid of gloss and, when examined under a lens, exhibits a serrated or toothed surface, which is eminently suitable for the successful application of a succeeding coat. It is evident that a hard-drying, full-bodied varnish, rich in gum resin, must be employed as an undercoating or flatting varnish. The relative proportions of gum resin to oil to form such a varnish are not fixed, several factors contributing to the hardness of the dried film, but it may be stated that they are more nearly equal than in varnishes used as a finishing coat.

A further function of the undercoat is to act as an additional cement or binder of the surface cells of the wood, and to protect them against penetration of moisture before the finishing coat has had time to attain its maximum water-resisting power. It is of importance that the undercoat should be sufficiently hard before the finishing coat is applied, otherwise blistering may be produced owing to volatile products or vapours, imprisoned by the finishing coat, causing distension of its surface.

Having thus obtained a sufficient body or thickness of varnish, the finishing coating may now be applied. In this also many factors have to be considered. A coating is required, which shall have a maximum gloss, which shall be of sufficient hardness to withstand the ordinary wear and tear to which the varnished article is to be subjected, and which at the same time will possess the requisite elasticity to withstand mechanical strain and changes of temperature, besides being weatherproof and waterproof. It is evident that varnishes for indoor use need not possess the degree of elasticity and resistance to weathering required for outside varnishes. The question as to the hardness of the dried film is determined essentially by the nature and amount of the gum resin used in making the varnish. It is evident that the softest resins,

e.g. rosin, unless in the form of a metallic resinate, would not adequately fulfil such a condition. Elasticity will be determined by the relative amount of oil present, and to secure the optimum effect the minimum amount of the hardest gum obtainable ought to be employed. The questions of impermeability to water and resistance to atmospheric effects (oxidation beyond the limit necessary to yield a satisfactory wearing film) are an intricate problem, and it is the obtaining of such results that constitutes the art and skill of the varnish maker. The use of China wood oil has been of great assistance in obtaining varnishes with a low water absorption. In connection with stability to atmospheric effects, it is evident that for a given proportion of oil in any two varnishes the one which dries more rapidly will be the first to deteriorate on exposure, because the oxidation of the film has been pressed so far that the peroxides of the oil are more prone to be broken down (*cf.* action of driers, page 42). Moreover, superficial drying is apt to leave a soft undercoating, and the surface crumples up or "rivels" owing to differences in density and volume changes.

It is therefore advantageous to restrict the amount of drier to a minimum to secure a reasonable rate of drying. When considering the purpose for which a particular varnish is required, it is important to remember that the proportion of the constituents must be carefully adjusted; for example, a high degree of elasticity would not be required in a varnish which is to be kept immersed in water, whilst a considerable degree of impermeability would be demanded.

After this general account of the scheme of application of varnishes, it is advisable to consider the stages in detail.

The Application of Varnishes.—Varnishes may be brushed on, flowed on, or the articles to be varnished may be dipped in the fluid, or the varnish may be sprayed on to the surface. For decorative indoor work where special attention has to be paid to the surface, brushing on is generally adopted. Flowing on, or pouring the varnish on to a surface and allowing it to drain off, is confined to very elastic mixings which can be easily distributed over the surface. Dipping is generally adopted for dealing with articles for ornament or for surfaces which can be completely immersed in varnish, *e.g.* bedsteads and cycle frames are coated by a dipping process. Special attention has to be paid to the viscosity of the varnish to ensure the best surface, and this will depend on the composition of the mixing. The dipping viscosity is generally less than that for brushing. Application by means of spraying is now general, the varnish being delivered from a fine nozzle in the form of spray by means of compressed air. Provided that proper attention be paid to the viscosity, elasticity and to the temperature of the varnish, it is easy to obtain a uniform surface by the coalescence of the spray globules. There is also an advantage caused by the aeration of the varnish, which tends to a more intimate contact with oxygen than is the case in brushing or dipping.

Varnish Brushes.—Varnish brushes ought to be of good quality and stamped with the maker's name. A really good brush will last for many years if properly looked after, and new brushes are not required for every piece of new work. They may be flat or oval in shape; the bristles should be wire-bound, not string-bound. The bristles should consist of stout selected white hog's hair, ground or bevelled at the end, so as to prevent deep grooves being formed in the varnish, which may not flow out to a smooth surface. The condition of the bristles will be considerably improved by being used in japan or in colour before being used in varnish, so as to wear down the roughness of the ends of the bristles. They should be all of the same thickness, and stout or unsplit bristles should be removed by cutting them off close to the stock. They range in sizes from 4's to 6's. The secret of keeping brushes in proper condition is to hang them in a liquid, in such a way that the points do not reach the bottom of the vessel. The liquid may be turpentine, which is said to destroy the elasticity of the bristles, linseed oil, or, better still, some stock elastic varnish.¹⁰

Dipping.—The advantages of applying paint, japan, enamel, or varnish by an immersion process is obvious. There is great saving of time with a comparatively simple plant. Iron bedsteads are dipped in a tank of black japan and transferred to a travelling chair which carries them to the oven, the superfluous japan dripping off during the transfer. Thin coats are necessary, because if an attempt were made to make the coat thick, it would result in unsightly runs, fat edges, etc. It is usual to cover with vaseline the parts which are not to be coated; after the paint is dry, the vaseline and the paint over it can be easily wiped off, leaving the surface quite clean.

Spraying.—The principle of the method is to use compressed air, at a pressure of 20-50 lb. per square inch, supplied from a compressor. The concentric jet form of sprayer is now almost universally employed where painting, enamelling, or varnishing is carried out on a large scale. The advantages are many, and they produce the greatest effect with the least possible consumption of air. The smallest work, *e.g.* jewellery, or the largest, *e.g.* gasometers, can be coated at a speed about four to ten times that of application by the brush. The amount delivered may be regulated from what would be applied in a single stroke by any brush from quarter-inch to four-inch size. The principal object is to apply the paint until the globules coalesce. Too much would make the paint or varnish run, too little would leave the surface uncovered. There are no brush marks. The air pressure required varies with the consistency of the paint and its viscosity. Thin lacquers and varnishes may be sprayed with 18-20 lb. air pressure, and up to 50 lb. will serve for most classes of paint. The volume of air used varies from $1\frac{1}{2}$ cubic feet per minute for varnishes to 8 or 9 cubic feet for paints. The air is also employed for other purposes; *e.g.* a small amount is used to provide a pressure feed of colour or varnish to the instrument. Where a heater is employed a small

amount of air is by-passed through the pistol to keep it warm when the spraying is momentarily stopped.

There are a number of types of spraying apparatus in use, of which a few may be mentioned, such as the Aerograph, the Aeron, and the Aerostyle. These three are of the concentric jet type.

The Eureka spraying machine, the Invincible, the Midland sprayer, and the Paasche air brush are other forms.

The Aerostyle (Fig. 30) is of pistol shape, and is supplied with or without pressure feed accessories. It may be used for all general painting or japanning. The adjustment of the nozzle for wide or narrow sprays can be locked in position by means of a small ring. The diagram shows the details of construction of the spraying pistol. The air supply is admitted by a trigger. The adjustment of the pistol for working is as follows: Release screw 14 on cross head 13, and whilst the instrument is connected with the air supply, slightly withdraw the trigger 12, allowing a small amount of air to pass through the nozzle. Whilst maintaining the trigger in this position, move the cross head along the needle until it bears against the cam 10, and in this position clamp the same by screwing home the clamping screw 14. If a wide spray is required the nozzle 8 is unscrewed to a small extent and then locked by means of a small ring 8a, but if a narrow spray is desired, the nozzle 8 is screwed on further and locked in position. On all round work one position serves, *i.e.* a position in which the recessed point of the nozzle coincides with the end of the tip 9, which just allows the needle 5 to project through it. If foreign matter becomes lodged in 9, the varnish or colour bowl 2 must be disconnected and the nose 4 removed and the parts cleaned with turpentine. Special spraying cabinets with suitable ventilation are provided, the form depending on the class of work. Painters are equipped with masks to prevent inhalation of the fine spray. One man can apply as much paint as three brush hands, and two men can put on 50 gallons of paint in one day, using well-regulated sprayers. Full details respecting spraying plant are given by authorities mentioned at the end of the chapter.^{11, 12}

The advantages of spraying over brushing are essentially those of time saving: also, if the machine has been carefully adjusted to give proper delivery, the surface is fuller, of more even thickness, and free from brush marks. Moreover, this fuller coat often means a reduction in their number, but the hardness of the undercoats may be diminished by the increased thickness in the layer. A mottled appearance on sprayed work is due to the paints not having been specially prepared for spraying, or the varnishes not being of suitable elasticity, and the media used drying too quickly, thus preventing the enamel from flowing out satisfactorily. It may be stated that spraying tends to reduce the faults of a paint or varnish rather than to accentuate them.

Flowing Off.—This process is largely used in the enamelling and painting of automobile bodies. A great saving of time results,

and it is stated that the "life" of the painted or enamelled surface is prolonged.

The process as carried out by the Ford Motor Car, Co. consists

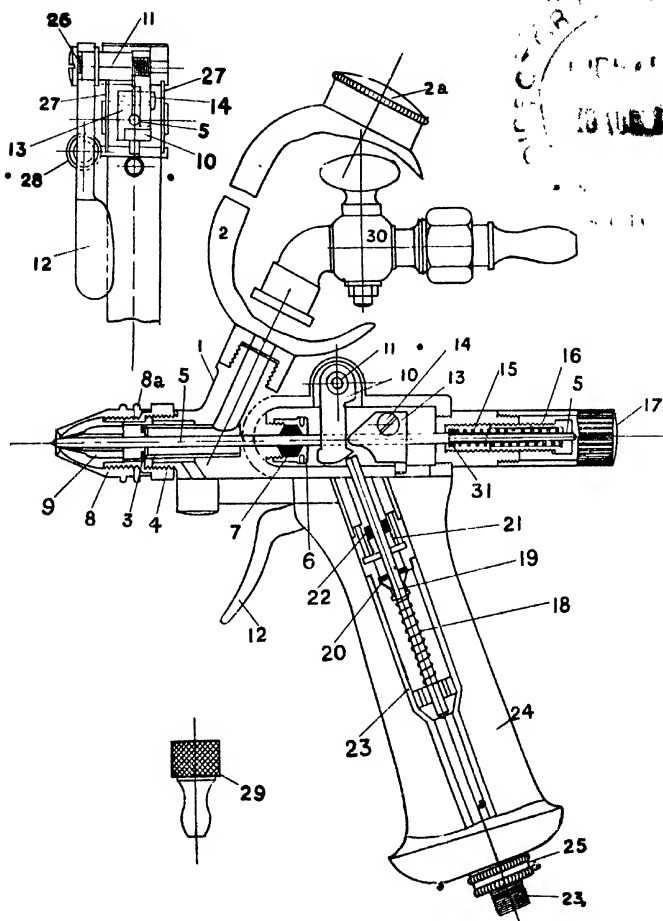


Fig. 30.—Acrostyle pistol paint sprayer.

in coating the body with blue-black enamel by gravity only, *i.e.* the enamel is placed in an elevated tank and is delivered on to the work through a flexible pipe and slotted nozzle opened by a lever, which is actuated by the thumb of the operator. No spraying

is required, and dipping is out of the question, as only the exterior of the body is to be enamelled. Each coat takes two minutes to apply to the whole surface of a four-seater Ford motor body. Formerly the undercoats were sprayed on the work in the ordinary manner, and the finishing coat of varnish was flowed on by the gravity method. The undercoats are now flowed on with quite a satisfactory result. The modification causes more paint to adhere than would have been applied by spraying, and it is found that one coat may be dispensed with. There is also less rubbing down because of the smoothness of the coat produced, and the time of application is reduced to two minutes. Nevertheless some authorities consider that the spraying of undercoats gives better results than the "flowing on" method.

The car body is mounted on a platform fitting in a V-shaped trough which surrounds three sides of the body, and is slightly inclined to allow the superfluous paint to run off through an orifice into a receptacle. There is a series of four troughs and tanks corresponding in number with the coats to be applied. After the application of the undercoat the bogie supporting the car is wheeled into a stove and kept there for an hour at 160° F. The surface is then rubbed down with fine glass paper and moved to the second trough for the application of a more glossy undercoat, which is stoved and rubbed down with pumice and water applied by felt pads. The third coat is then applied, stoved, and rubbed down, and finally the fourth or varnish coat is applied, which is air dried. The output from this department is 70 cars a day. The varnish is applied in a separate room from that used for the application of the paint. The requirements are stringent as to the quality of the paint, enamel, or varnish used. It must be sufficiently viscid to adhere to the surface, sufficiently fluid to run off freely without leaving runs, tears, or "fat edges," and it must flow out uniformly. In fact, all the conditions requisite for a dipping paint-enamel must be realised, and the varnish must flow out and yield not too thick a coat, which would be likely to lead to blemishes.

The Floco Process.—This process is in some respects similar to the above, but it is intended primarily for the application of varnish by flowing it over a spray-painted surface. The varnish, instead of being discharged by gravity, is pumped from a tank.

The varnish is pumped by an electric motor-driven (1-6 h.p.) pump in a continuous stream through a flexible hose to a delivery nozzle. The flow of the material is adjusted by a regulator adaptable to any class of work and viscosity of fluid without changing the speed of the motor. When the nozzle is closed, the material pumped in is forced back into the tank through the overflow, which serves to agitate the material, especially if it is an enamel containing pigment. The body to be covered is placed over a drained trough and the varnish applied to the upper part and allowed to flow down. Sufficient material is applied to ensure perfect flow to the bottom of the work. The drainings accumulate in the trough and run back into the tank. The tank holds 15 gallons, and the nozzle

will operate successfully with 1 gallon of varnish. The pressure tank in this equipment permits of the use of heavier or more viscid enamels and paints than is possible where gravity alone is depended on.¹²

The Stoving of Varnishes.—*Gas and Superheated Water Stoves.*—

The details of the construction of japanning stoves are often neglected. In some cases they are heated by open gas jets, which cause discoloration, and are objectionable even when black japans are stoved, as the presence of gas fumes retards oxidation. In

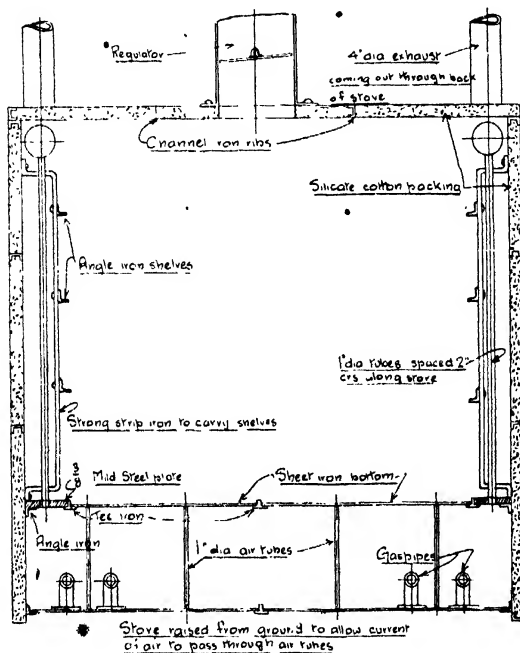


FIG. 31.—Varnish stove.

the Perkin system water is heated under pressure and comparatively high temperatures are obtained in a simple but efficient manner. Coils containing the heating water are placed inside the stove. The oven should be properly ventilated to allow proper oxidation.

W. Goodyear & Sons, Dudley, supply stoves (Fig. 31) heated by gas (ordinary lighting or producer), steam, superheated water, and oil, either single, double, or treble cased, suitable for all purposes and all articles and giving a temperature up to 350° F. In the Duplex gas and superheated water stoves there is a patent dual heating arrangement, the advantage of which is that, should only

a small amount of enamelling work be dealt with, one stove can be worked independently of the others without the trouble of getting the boiler ready. The superheated water system is only economical when enamelling is conducted on a large scale, as boilers and furnaces are necessary. Four large stoves is the minimum which can be worked successfully by the hot-water system. The gas-pipes are at a lower level than the hot-water pipes. The temperatures required will vary with the work: for black japons either 180°-200° F. or 250°-350° F., gold stoving up to 200° F., polishes about 140° F. During the stoving there is always discoloration. In stoving of varnished furniture or piano panels, it is advisable to have present a sufficient humidity in the air in the stove to prevent subsequent warping of the wood.

Electric Stoves.—Mention may be made of the description of electrically-heated drying ovens or stoving ovens for paints, varnishes, japons, and enamels. W. J. Scott¹³ states that any suitable number of units of the ribbon-type heaters of 25 kilowatts at 120 volts may be installed. An installation consists of one or more heaters connected with a two-wire circuit controlled by a knife switch; a three-wire single phase or even a three-phase circuit may be used. Details are given for filling up the oven and controlling the temperature so as to ensure safety of working. Recent developments are described by M. R. Armstrong,¹⁴ who shows that for an oven temperature of 200° C. a temperature of 54° C. was maintained on the outside walls under ordinary conditions. For 55 motor-chassis 12 gallons of enamel were used for fifty minutes' stoving period. The average hourly consumption was 213 kw.hr. for six chassis per hour.

The Drying of Varnishes in Air. A drying room ought to be kept at about 70°-75° F., be dust-free and well ventilated, with a good upper light if possible. The atmosphere of the room ought to be kept dry, and the doors closed, so as not to disturb the dust. Different varnishes have their special peculiarities in behaviour on drying; some come to a tack quickly and harden off slowly, others set slowly, but harden off quickly. The presence of excess of manganese driers in a varnish causes superficial drying, whereas if lead is present the drying is uniform throughout. The action of manganese driers is more sensitive to changes of temperature than that of lead driers. The time of drying is determined by the craftsman, and corresponds roughly to a dust-dry stage, when dust will not adhere to the surface, and when the finger drawn lightly over the surface no longer produces any mark.* It is a crude method with about one quarter of an hour error. Much has been said about the precautions necessary to ensure satisfactory air-drying. A few of the hints for workmen may be enumerated: A varnish may go wrong through the undercoat being improperly prepared and not in a condition to receive a finishing coat; this may be due to solvent action on the imperfectly hard undercoat

* H. A. Gardner has devised an apparatus for determining the time of drying of paints, varnishes, etc., to an arbitrary but definite degree of drying.¹⁵

or to chemical action between the components of the layers. If a varnish be applied in a badly ventilated room, the setting of the film will be much retarded. Moreover, application in a hot room which becomes cold at night will give rise to imperfections of the surface; this is due to separation of the components before the film has had time to set properly. Similarly a varnish will go wrong if it be kept in a cold place and then applied in a warm room without proper preparation. Many varnishes are in an unstable condition, and a fall of temperature often causes a partial separation of the resin-oil components. The influence of the humidity of the air on the surface of a varnish film is of importance; e.g. a varnish is almost certain to go wrong if water be sprinkled on the floor of a room with the object of settling the dust which might be caught in the drying varnish.* The absorption of water during the drying of the film may give rise to a subsequent cloudiness of the film, which will be referred to under "Bloom." In summer a varnish dries quicker than in winter, but it hardens more slowly. The warning that a gas cooker must not be used in any part of the house where varnish has recently been applied until it has thoroughly hardened off, has its explanation in the absorption of moisture and acid fumes arising from the cooker by the varnish film. Substances evolving ammoniacal vapours will produce the same effect as fumes from a stove.

In order to understand these warnings for the craftsman, consideration of the general properties of the drying oils must be borne in mind. Free escape of the thinners requires good ventilation, which also accelerates the catalytic oxidation. A rise of temperature of 10° C. will double the rate of oxidation. A fall in temperature or chilling will prevent the diffusion of oxidation products into the film, causing inequalities in its upper and lower parts, due to the different densities of the oxidation products compared with the unoxidised components. The production of separated particles of resin-oil is manifested in a pinhole-like appearance. The films of many varnishes are often strongly water-absorbing, so that the surface becomes charged with a film of water and dust which may set and is difficult to wash away. Moreover, such a film retards the hardening off of the varnish, and in fact softens it. The old custom of washing the surface to harden it is quite sound, because it removes the adherent absorbing film of moisture-saturated dust.¹⁶ Too rapid escape of the solvent medium is conducive to striated and ravelled surfaces.¹⁷ An excess of drier, especially manganese, will give a striated surface owing to uneven oxidation of the film. Some observers maintain that oxidation and polymerisation proceed during the oxidation of the film. Wolff¹⁸ maintains that oxidation and polymerisation proceed at rates depending on the wave length of light to which the varnish is exposed (see page 16). Further details as to the behaviour of varnishes when drying in the air will be given under the Defects of Varnishes.

* If the moisture content of the air does not exceed 70 per cent saturation no harm will result (page 236).

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14. M. R. Armstrong, *Elec. Journ.*, 1921, **18**, 6, and *Chemical Abstracts*, 1921, **15**, 604.
15. H. A. Gardner, Circ. 167, *U.S. Paint Manuf. Assoc.*, Feb., 1923.
16. A. S. Jennings, *The Painters' Pocket Book*, 1921, p. 84.
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CHAPTER XIII

TYPES OF OIL VARNISHES

A GENERAL description of the manufacture of a typical oil varnish composed of gum, resin, drying oil, siccativ, and volatile thinner has been given in preceding chapters. It is not the intention of the writer to supply details of the composition of the various types, except in a general way. Each manufacturer has his own formulæ, uses special materials, and works under special conditions, which may or may not be in reality common to all. At any rate, he protects the secrets of his own business, which is only right and proper. The writer's experience of published formulæ is that they are correct as far as they go, but they are not to be considered as recipes of manufacture, and they merely illustrate broad differences between types or varieties of varnishes.* The number of varieties of varnish made by manufacturers is great. One firm lists as many as two hundred, each having its own special use. There is no general classification of oil varnishes; probably the most generally accepted is that of long-oil and short-oil. An American writer will indicate sixteen classes, a French writer will quote twenty-four types, while a German writer will give one hundred and seven varieties classified according to the hardness of the resin used and the proportions of resin to oil. The important classes may be given as decorator's varnishes for inside and outside work; furniture varnish, including cabinet varnish; coachbuilder's varnishes, including carriage, motor, and railway work; boat, marine, or spar varnishes; stoving varnishes, polishes, and black japans. There are also many varnishes for special purposes.

Decorator's Varnishes.—These varnishes, as their name implies, are intended for use by the house decorator. It is not expected that they should be subjected to such severe conditions of exposure as in the case of coach- or motor-body varnishes. With the exception of gold size or preparation varnish already referred to, they are characterised by a fair degree of elasticity and moderate speed of drying.

Church Oak is a term usually applied to a varnish yielding a specially hard film, which does not soften appreciably at tempera-

* The formulæ given in Andés' *Rezeptbuch für Lack- u. Farben-Industrie*, III. Aufl., 1922, are an illustration of this statement.

tures up to 40° C., and so can be used on seats. The hardness of the film is often obtained by the addition of lime to the gum-oil combination, a calcium resinate of high melting point being formed. Much depends on the quality of the resin used, which must be present in sufficient quantity to impart hardness and at the same time not to reduce elasticity. The index of refraction of a varnish is stated to be higher than that of its component parts (Sabin), and skill in operation will produce a brilliant varnish with a larger proportion of oil and increased elasticity. There are so many variables that no two varnishes from different sources will be alike. A German variety of church oak (Kirchenstuhlack) may contain gum-resin and oil in the proportions of two to one, but such a mixing, although hard, would lack elasticity and be liable to crack. It is possible to obtain a more satisfactory coating containing a much larger proportion of oil with the requisite hardness and elasticity.

Floor Varnish, *Vernis pour planchers*, is softer than church oak. It is similar to flatting, but need not be rubbed down, and will not bloom. The proportions of resin to oil may be 12 to 18 galls. of oil per 100 lb. resin, but they vary in different countries. In France the proportions of gum to oil are 24 : 27, or 26 : 26, with the addition of driers and thinners, according to the manufacturer's own methods. A German floor varnish may contain copal and oil in the proportions of 10 : 5 or 7 : 5. The floor is previously stained with an oil stain which sinks into the wood, and is then varnished over. Such a varnish ought to dry over-night. A spirit varnish may be used, but it lacks the durability of an oil varnish.

Flattening Varnish, *Vernis flattung*, *Schleiflack*, is used extensively in some countries as a finishing varnish for wood, especially in climates where bloom does not form. The proportions of resin and oil in France are : 25 kilos Congo copal, 25 linseed oil, 50 kilos thinners, with 1.7 kilos of lead linoleate, 1 kilo of dried sulphate of zinc, and 0.35 kilo of manganese resinate. In a German flattening the proportions of copal to oil may vary between 10 : 7.5 and 10 : 15. In England flattening contains resin and oil in the proportions of 60 lb. : 8 galls., with about 11 galls. of thinners. Flattening varnish is used as an undercoat, drying quickly to give a hard surface, so that it may be rubbed down about twelve hours after drying to give a dull surface which will not sweat up, *repousse au gras*, on standing. The addition of the finishing coat on the rough, hard, flattened surface provides a satisfactory adhesion of finishing and undercoats. It is not expected that flattening used as a finishing coat will have durability on exposure; also it is liable to bloom.

Front Door Varnish must combine elasticity with hardness, and will contain more oil than furniture varnish (10 parts copal with 15 parts oil, by weight). It must be free from bloom.

Inside Varnishes.—For inside varnishes manila copal, or one less hard than Congo or Zanzibar, may be employed, and the proportion of oil is higher than in flattening or church oak. Coffignier's figures may be taken as fairly typical, except that Congo copal is preferred to manila.

Manilla Copal.	Linseed Oil.	Thinners.
22	33.5	44.5
22.5	39	40

The driers are peculiarly French; *e.g.* 1.5 kilos lead linoleate, 0.75 kilo dried sulphate of zinc, and 0.375 kilo manganese resinate. Inside varnishes must have satisfactory hardness and gloss, but not necessarily great weather-resisting power. These varnishes must be considered from a decorative standpoint as well as from a protective standpoint. A decorator insists upon lustre and flow and absence of "bloom" on the film. The requirements for a protective coating are set out in the British Aircraft Specification 2 X. 7 (1920), which may be summarised as follows:

The varnish shall be clear and bright and shall be manufactured on an oil basis. The viscosity, when determined by means of an Ostwald viscometer at 25° C., shall be between 30 and 55 when compared with glycerine (100), see page 257. The varnish, when "flowed on" to a glass plate, shall dry at 70° F. (21° C.) in not more than eight hours. The film produced when the varnish is flowed on to a glass plate and allowed to dry for twenty-four hours at 70° F. (21° C.), and subsequently heated for two hours at 212° F., shall show no signs of brittleness when scratched with the point of a pen-knife.

The film produced on a glass plate and allowed to dry at 100° F. in an atmosphere charged with burnt coal gas shall not web or wrinkle to any appreciable extent (see page 248).

Mixing Varnish.—This is specially intended for imparting gloss to oil paints, so that it should have as low an acid value as possible, otherwise "feeding up" with basic pigments may occur.

White Oil Varnishes are made from the palest gums and oils for application on delicate colours.

Crystal Paper Varnish is a dammar varnish which is almost colourless, and is used for application on wallpapers, etc.

Furniture Varnish.—This variety is of variable composition. It is no use supplying material which will last longer than the furniture, so that the introduction of ordinary resin is very common. The proportions of resin to oil in America are 100 lb. of resin and 12 to 15 gallons of oil.

In Germany the proportions of gum to oil are 10:15. In re-varnishing furniture, a number of thin coats of a varnish made by incorporating 100 lbs. resin with 15 to 20 gallons oil are applied, rubbing down between each coat until the requisite brilliance is obtained. The varnish must be free from bloom, and for that reason some authorities state that the copal must be carefully selected, and that no thick acid oil must be used in the manufacture of high-class varieties.

	Manillakopal.	Lackleinöl.
Innenlack, Möbellack, Dekorationslack . . .	6	5

Cabinet Varnishes are hard and quick-drying, with large resin content giving a high gloss, but with no weather-resisting properties ; moreover, they are liable to bloom.

Coachbuilder's Varnishes.—These represent the highest art of the varnish manufacturer, and are characterised by careful preparation, long maturing, special selection of gum resin and of oil ; the nature and proportion of driers will vary according to the purpose for which the particular varnish is destined. None but specially selected pale hard resins and carefully treated oils would be suitable for the pale varnishes known in the trade as French Oil, Maple and Venice Body Varnishes. The terms "body" and "carriage" referred formerly to the application to the body (doors, roofs) and the under portion (wheels, etc.) of coaches. Such varnishes used as finishing coats must be dust-dry in twelve hours. They must give no deposit on standing ; their films must be free from bloom, must retain their lustre on weathering for several years, and must not crack. The undercoating varnish (hard body) ought to dry in ten to fifteen hours, preparatory to being rubbed down for the application of the finishing coat. The general composition is essentially the same in English, American, French, and German factories, although the qualities are often widely different. In England the general formulæ may be summarised as follows : ¹

	Gum.	Oil.	Thinners.
	Lb.	Galls.	Galls. (approx.)
Finishing body	60	15	15
Elastic varnish	60	12	13
Hard elastic varnishes . .	60	10	12
Quick hard drying . . .	60	5-6	12
Polishing hard drying . .	60	2-3	14

For an American rubbing varnish (for the undercoat), 100 lb. of gum are incorporated with 6 to 12 galls. of linseed oil. A French finishing varnish may contain 16 parts of hard resin, 42 parts of oil, and 42 parts of thinners, together with 2.25 parts of lead linoleate, 1.125 of dried sulphate of zinc, and 0.66 of manganese resinate.

Formulæ for elastic outside varnishes are given by Coffignier as follows :

	Resin.	Oil.	Thinners.
	Kilos.	Kilos.	Kilos.
Vernis à caisses . . .	20	40	40
Vernis à trains . . .	21	47	32
"	16	38	1.1 litharge, & 0.70 MnO ₂ 46
"			2, lead linoleate, 1, copperas (dried), 0.5 Mn. resinate

Vernis à caisses corresponds to finishing body. Vernis à trains corresponds to the hard elastic varnishes mentioned above.

The proportions given in German literature for body varnishes are as follows :

	Resin.	Oil.
	Kilos.	Kilos.
Güterwagenlack, Maschinenkopallack .	10	16
Kutschenlack	10	15-20
Lokomotivlack	10	10
Kutschenlack (schnelltrocknend) . .	10	10

It is recommended that no lead driers should be used in finishing body varnishes (Seeligman and Ziecke). A French specification for motor-coach work states that oil treated with lead should not be used. The presence of lead in the form of an oil soap will tend to produce chalkiness on exposure to rain, but it will tend to reduce bloom. Another formula for varnish for railroad coaches² is given as follows : resin 10, linseed oil 15, stand oil 0.5 ; driers : lead and manganese resinate 0.5-1.0, lime 0.1-0.25, turpentine 20-35 kilos.

It is evident that by blending hard body varnish with finishing body, desired grades of hardness can be obtained. A firm may offer fourteen varieties of coachbuilder's varnish, each with its own special functions.

From the standpoint of a protective coating for external woodwork, the British Aircraft Specification (2 X. 6, 1920) requires a rate of drying of eight hours at 70° F. (21° C.) on glass. The dried film shall be "hard dry," *i.e.* in such a condition that a second coat of varnish could be satisfactorily applied in not more than forty-eight hours after application. A film of the varnish on a panel of 30 S.W.G. tinned iron, after air-drying for twenty-four hours at 21° C., stoving at 100° C. for two hours and allowing to cool for one hour, shall stand bending over a $\frac{1}{8}$ in. diameter rod without cracking at the point of bending. The viscosity at 25° C. shall be 32-65 (glycerine = 100, *s.g.* 1.26 at 15° C.). A film of the varnish on a clean glass plate when dried at 38° C. (100° F.) in an atmosphere charged with burnt coal gas shall not web or wrinkle to any appreciable extent.

Tests for resistance to water, lubricating oils, and petrol :

Durability.—The varnish shall produce a film sufficiently durable to withstand for at least six months the deteriorating effects of ordinary weather and service conditions.

Resistance to Lubricating Oils.—The varnish shall be applied to a glass plate and allowed to dry for seven days at room temperature, after which time the plate shall be immersed in the lubricating oil (castor and/or mineral) for two hours at 125° F. (52° C.). It shall then be removed from the oil and wiped with a soft rag moistened in petrol. The film shall not be permanently injured by this treatment.

Resistance to Petrol.—The varnish shall be applied to a glass plate and allowed to dry for seven days at room temperature,

after which time the plate shall be immersed in petrol for fifteen minutes. It shall then be removed from the petrol and allowed to dry for thirty minutes. The film after this treatment shall regain its original condition and appearance.

Varnishes for Special Purposes.—This class includes boat, yacht, and spar varnishes, which are specially prepared to withstand immersion in water; filling and priming varnishes, and gold sizes, which have been already referred to under fillers (page 217); stoving varnishes for the protection of metal plates where rapid application and great hardness are essential; polishing varnishes intended for decoration of articles not exposed to the weather, in which the finish is obtained by hand-polishing the dried film.

Boat Varnishes.—A boat varnish should give a film impermeable to water, able to withstand the action of the sun and weather, and not turned milky on immersion in water. Elasticity is essential, and China wood oil is becoming more and more a component of these varnishes. An American spar varnish, which is used for coating the woodwork not directly in contact with the water, contains 25 galls. of oil per 100 lb. of resin. From what has been stated with regard to the water absorption of varnishes, the presence of lead with non-polymerised linseed oil is undesirable, and a high percentage of resin, although increasing the water-resisting power, will deprive the coating of the necessary elasticity to withstand changes of temperature. It is evident that polymerised oil will be an important component. Abstracts of specifications (English and American) will show the requirements of seaplane, boat, and spar varnish.

Seaplane Varnish.—The British Standard Aircraft Specification X. 17 (1920) requires that the varnish shall be clear and bright and shall be manufactured on an oil basis. It may be supplied as undercoating and finishing varieties. The viscosity shall be between 35 and 65, as determined by means of an Ostwald viscometer at 25° C. (glycerine = 100). The varnish, when flowed on a glass plate, shall become "dust-dry" at 70° F. (21° C.) in not more than twelve hours for dual-coating varnish, eight hours for undercoating varnish, and fifteen hours for finishing varnish. In the latter case the test shall be carried out both on the finishing varnish separately and over the dried undercoating varnish.

The film produced when the seaplane varnish is flowed on a glass plate and allowed to dry for twenty-four hours at 70° F. (21° C.) shall be glossy, elastic, and free from blemishes, and shall retain these properties for at least six months under service conditions. The elasticity, webbing, and resistance to petrol and oil have already been described under the requirements for outside varnishes.

Resistance to Water.—The following conditions have been proposed by the writer: Weighed glass or aluminium plates are completely immersed for 1 min. in the varnish at 20° C., and then withdrawn at a uniform rate of 1 in. per 10 secs. by means of wire passing over a frictionless pulley. The varnished plates are allowed

to drain at the ordinary temperature for eight hours and stoved in an electrically heated stove at 48°-54° C. in a current of air (5 litres per hour) until constant weight is obtained. The plates are completely immersed in N/400 NaCl. aq. (distilled water is unsuitable), and weighed after three days' immersion. Before weighing the plates are lightly pressed between blotting-paper to remove adherent water. The gain in weight of the varnish film must not exceed 8 per cent, and the film must remain clear during the immersion.

The American specification³ for a spar varnish is fuller in detail and more stringent. The additional requirements may be summarised as follows: *Colour*—Not darker than a solution of 6 grams potassium dichromate in 100 c.c. sulphuric acid (s.g. 1.84); *Flash point*—Not below 35° C. (95° F.); *Non-volatile matter*—Not less than 40 per cent by weight. It shall set to touch in not more than five hours, and shall be dry and hard in not more than twenty-four hours.

Water Resistance.—The dried film must withstand cold water for eighteen hours and boiling water for twenty minutes without whitening or dulling.

Working Properties.—Varnish must have good brushing, flowing, covering, and levelling properties.

Toughness.—The film on metal must stand rapid bending over a rod 3 mm. ($\frac{1}{8}$ in.) in diameter at 70°-80° F. Full details as to the Laboratory Examination are given in the Circular mentioned in the reference at the end of the chapter.³

Stoving Varnishes. These varnishes are required especially by tin box makers. They are stoved at 140°-400° F., the time and temperature varying according to the kind of varnish and the local conditions. If the plates be decorated with light colours these would darken if heated too strongly. In other cases speed is the important requirement. It is therefore necessary to produce a variety of varnishes to meet the varying conditions. The requirements are essentially great hardness and elasticity to stand stamping. Gold stoving for tins must often be able to resist the action of boiling water and steam without deterioration of the surface or detachment from the metal. It is evident that they must be on a good copal linseed oil basis, or, if great water-resisting power be required, a varnish on a wood oil basis is advisable.

Plano and Polishing Varnishes.—French polishing with a shellac varnish is being replaced by special hard oil varnishes, which give a lustrous finish, resistance to sea air and to extremes of heat and cold, and which, unlike shellac, do not crumble or peel off. Besides the great shortening of the process, much less skilled labour is required in their application. The preparation of the wood previous to applying the varnish is more elaborate than usual. It is first carefully cleaned and planed, and an oil wood-filler is applied in the form of a paste thinned to the consistency of a paint with turpentine and well rubbed in against the grain of the wood. If the pores of the wood are fine a single treatment is sufficient, but with coarser-grained wood, e.g. oak and American walnut, the rubbing in must be repeated. The filler must be applied so as to

leave an even surface of wood, free from particles of the filler ; as it contains a little varnish, drying in about ten hours, the mineral matter of the filler is bound in the pores of the wood (see page 217). In the American process the polishing varnish is applied directly on the prepared surface, but the German custom is to impregnate the filled surface with a solution of shellac or collodion. Many woods, such as maple, beech, and lime, are not filled by the oil wood-filler, and require further impregnation. The prepared surface is lightly rubbed over with sand-paper before varnishing. The varnish must be of the best quality, must dry hard in about twenty-four hours, and be free from tack ; moreover, it must be hard and elastic, and must yield to the expansion and contraction of the wood. It must stand superficial polishing and be neither too brittle nor contain too much oil, whereby its lustre would be reduced on polishing. In some schemes one coat is applied daily until four coats have been brushed on. The varnish must dry in air in from one to one-and-a-quarter hours at the ordinary temperature.

The drying room must be dust-free, and the air should be previously washed and warmed and its moisture content maintained at 60 per cent saturation. The presence of moisture prevents the varnish from forming a skin, which would retard the evaporation of the solvent, and permits of complete oxidation. The percentage of moisture must not rise above 70 per cent saturation, otherwise condensation may ensue and impart a net-like pattern to the surface. Oval and broad forms of varnish brushes are used. It is not advisable to allow the worker to add thinners to the varnish independently, as it is of importance that the surface should be free from defects. After adequate hardening the film is flattened down with felt and water and pumice, but not so strongly as to cause small depressions in the film. The surface is then washed and dried with chamois leather. Next day a second coat of varnish is applied and after twenty-four hours rubbed down with water and rotten-stone. The surface is now semi-lustrous, and in order to give a high lustre it is polished with a cotton-wool ball saturated with a polishing liquid, or with chamois leather and fine Vienna chalk and petroleum. If four coats of varnish be applied, six days are required for the whole process, because the work is allowed to remain for two days after varnishing before being hand-polished. Another scheme consists in applying three successive coats, each of which is stoved in a damp atmosphere for ten hours at 80°-90° F. The fourth coat is stoved at the same temperature, but in dry air. The work is rubbed down with fine pumice and water, using felt, and finally polished with oil and rotten-stone. The hardening of the varnish between the coats is of great importance.

In the German system Jäger recommends thinning the filler with collodion containing a soft resin, and after the varnish coating is applied, polishing the hard surface with sand-paper. Finally, the finishing coat is treated with a collodion thinning liquid, whereby its surface is hardened and rendered smooth. A dust-free room is unnecessary, but the lustre is not so good as in

the American process, and sand-papery is apt to cause fine scratches. Felgenauer (Allendolac polishing process) applies a film of collodion containing resin on the filled surface, then the varnish coating, polishing between each coat with sand-paper and water containing a small quantity of oily substance. The last coat of varnish is rubbed down with a polishing ball containing polishing oil, alcohol, and acetone.⁴ In the final polishing with a shellac varnish where a thin lac film is required, oil must be very sparingly used, and a little celluloid may be mixed with the shellac to impart elasticity.

Violin Varnishes.—The effect of varnish on the quality of a violin is a debatable subject. All that can be said with regard to the varnishes on famous violins is that they were of elastic resin-oil character. It has been stated that an oleoresin, *e.g.* Venice turpentine, dissolved in linseed oil was the basis of the Cremonese, Venetian, and Neapolitan varnishes (G. Fry, *Varnishes of the Italian Violin-makers*, 1904).

Matt Varnishes.—In order to reduce the gloss of a varnish surface, and at the same time to retain the protective properties and smoothness, it is customary to embody a suitable wax, *e.g.* paraffin wax, in the warm varnish. On cooling, the wax separates out, and it is advisable to warm and to shake before using, so as to ensure uniform admixture. Such a varnish consists of a thin size in which the white wax is suspended, *e.g.* 70 parts of gold size, 15 parts of turpentine, and 2 parts of white paraffin wax. Being thin, the varnish dries rapidly and gives a smooth matt surface. With the introduction of China wood oil the prospects of obtaining a matt varnish without paraffin were improved. The varieties containing paraffin could not be stoved. Many formulæ have been put forward as yielding good results, but the conditions of drying and stoving must be carefully complied with; excellent results are sometimes produced, followed by complete failure if the conditions be varied. Aluminium tungstates have been recommended in the form of an artificial alumina compound bound by saponification with the oil varnish. The following mixture has been suggested: 90 parts oil varnish and 4-10 parts basic alumina compound, such as alumina, its hydroxide, or a special basic aluminium silicate. These are rubbed together and the strongly thickened products diluted with thinner.⁵

Some matt varnishes contain carbonate of magnesia in suspension. The general principle appears to be the holding of the fine pigment in suspension by means of an emulsifying agent, or else to mix a suitably ground alumina compound with a varnish and apply it at once with a brush. In this case success will depend on the nature and fineness of the pigment. If a suitable emulsifying agent be employed, the mixing will remain permanently turbid without separation of the pigment.

Gold Size.—Gold size is essentially a priming, setting, and hardening varnish, and gives no highly lustrous surface. It can be used either alone or as a hardening drier when mixed with colours. The proportions of resin to oil are more or less the same in all

countries. A French gold size, according to Coffignier, may contain 17 parts of manila gum with 25 parts of linseed oil and 58 parts of thinners, with which are incorporated 8.25 parts of lead linoleate, 5 parts of dried zinc sulphate, and 1.7 parts of zinc resinate. A German pale gold size will contain 90.7 parts of resin for 130 parts of linseed oil, the same resin-to-oil proportions as in the French variety. The driers are added in the form of litharge (9.07 parts) and (22.7 parts) manganese dioxide, previously rendered soluble in the mixing by treatment with 9 parts of nitric acid and dried at 140° C.

The above relate to coach gold size, which ought to air-dry in about two to three hours. Japan gold size will be referred to under japans and bituminous varnishes.

An old formula for an English japanners' gold size is as follows: Two lots of 10 lb. aniini gum or hard copal are run with 2 gallons of oil; after addition of 10 more gallons of oil the whole is boiled well for two hours, with careful addition of 7 lb. of red lead, 7 lb. of litharge, and 3 lb. of copperas, and finally thinned with 30 gallons of turpentine. This gold size is stated to dry in ten minutes. A slower gold size for gilding purposes (gilders' size) is stated to consist of 8 lb. of copal, 2 gallons of oil, heated until stringy, to which 6 gallons of boiling oil are added, and the mixing thinned with turpentine. Some English gold sizes contain more copal resin and less lead oxide than in the above formula, the amount of lead oxide depending on the variety of size required.

Protection of Timber.—A specification for the protection of timber has been put forward by the British Engineering Standards Association,⁶ recommending precautions to be observed in treatment of the woodwork of aeroplanes, seaplanes, and flying boats. The scheme deals with materials for protection rather than for decoration, and includes treatment of internal (unexposed) and external (exposed) woodwork.

The materials shall be applied by means of a brush or spray.* In the case of "priming varnish" the application may also be carried out by means of "dipping." Care should be taken that the whole of the woodwork is completely covered with every coat, and no coat should be applied until the previous coat has been allowed to become thoroughly dry. The protective treatment should be carried out in properly ventilated rooms, the temperature of which should not be below 50° F. (10° C.), and preferably about 70° F. (21° C.).

Protective Treatment.

Class A.—Internal (unexposed) woodwork.

(a) Parts not coming into contact with doped fabric:

Procedure 1. There should be applied one coat of Priming Varnish followed by one coat of Internal Woodwork Varnish; or

* In the application of a short oil varnish by means of a spray, unless the varnish be warmed previous to application, a mottled surface is obtained. This does not occur when elastic varnishes are used (see page 222).

Procedure 2. There should be applied two coats of Shellac Varnish ; or

Procedure 3. There should be applied two coats of Transparent Nitrocellulose Varnish.

(b) Parts coming into contact with doped fabric :

Procedure 1. There should be applied one coat of Priming Varnish followed by one coat of White Dope-resisting Paint ; or

Procedure 2. There should be applied two coats of Transparent Nitrocellulose Varnish.

Class B.—External (exposed) woodwork.

Parts which are not taped :

(1) Using Varnish. There should be applied one coat of Priming Varnish followed either by two coats of External Woodwork Varnish or by one coat of Internal Woodwork Varnish and one coat of External Woodwork Varnish.

(2) Using Paint. There should be applied one coat of Priming Varnish followed by one coat of Undercoating Grey Paint and thereafter one coat of Aluminium Paint.

Parts which are taped (details as to the application of the tape are given in the Notes).—The two methods of procedure are as follows : (1) One coat of Undercoating Grey Paint followed by one coat of Aluminium Paint should be applied to the taped part. (2) One coat of P.C. 12 Varnish followed by one coat of V. 84 Varnish (2D. 103).

For the woodwork of Hulls and Floats the details of treatment of interior and exterior woodwork are as follows : (a) *Interior of Floats.* There should be applied two coats of Bituminous Paint. (b) *Exterior of Floats.* There should be applied to the woodwork one coat of Undercoating Grey Paint followed by one coat of Aluminium Paint. (c) *Interior of Hulls.* To the bottom of the hull and the underside of the fins there should be applied two coats of Bituminous Paint followed by one coat of Undercoating Grey Paint. To the remainder of the hull there should be applied one coat of Priming Varnish followed by one coat of Undercoating Seaplane Varnish and one coat of Finishing Seaplane Varnish, or by two coats of Seaplane Varnish when such a varnish is supplied as a single varnish for both undercoating and finishing coat. (d) *Exterior of Hulls.* (i.) Below the water-line. There should be applied two coats of Bituminous Paint followed by one coat of approved Anti-fouling Composition. (ii.) Above the water-line. (a) Using Varnish. There should be applied one coat of Priming Varnish followed by one coat of Undercoating Seaplane Varnish and one coat of Finishing Seaplane Varnish, or by two coats of Seaplane Varnish when such a varnish is supplied as a single varnish for both undercoating and finishing coat. (b) Using Paint. There should be applied one coat of Priming Varnish followed by one coat of Undercoating Grey Paint and one coat of Aluminium Paint.

Black Japans and Bituminous Varnishes.—These preparations occupy a special position, since they have for their characteristic ingredients a bitumen or asphalt. Both gum resin and oil may or may not be present, as the asphaltic substances differ far more widely in their hardness and elasticity than the various gum resins, and their properties can be modified with greater facility. The most important bituminous varnish in the higher branches of the decorative craft is known as black japan.* The method of preparation, specific choice of ingredients, etc., vary widely with different manufacturers. The specific purpose of black japan is in the production of a brownish-black ground of particular translucence or depth, thus differing from pigmented preparations (black enamel), which appear to reflect their depth of colour from the surface only. The main use of black japan in the coachbuilding trade is in the treatment of mud-guards, etc. The varnish is obtained by amalgamating specially treated oil of great drying power with suitable bitumens, in the same manner as described in the manufacture of copal varnish. The japan itself rarely possesses a great degree of elasticity or weather-resistance, so that it requires a coating of a suitable finishing varnish. The art of the varnish-maker consists in the preparation of a japan of great degree of depth and intensity of colour without employing so high a proportion of bitumen that solubility of the latter in the ensuing coat takes place, a condition manifesting itself by the appearance on the finished work of an undesirable greenish fluorescence.

The shade is difficult to control, and some japans give a chestnut-black coloured film, due to the variety of pitch used; the latter must be carefully selected and sweated to remove volatile bodies likely to interfere with the lustre and to leave the film tacky. The coating ought to stand polishing the day after application. It is difficult to give a general formula for these coatings, as the quality depends so largely on the selection of the materials. The components are hard resin, bitumens (natural and petroleum asphalts), and boiled oil and turpentine. The following formulæ may be taken as roughly representative :

Hard gum	25	11-17	20	} dries in the air in 24 hours. { Coffignier. }
Asphaltum or petroleum pitch	8-4	11-15-9	20	
Boiled oil	16-8	11-17-6	20	
Turpentine	49-8	11-17-6	20	

Another formula contains Egyptian bitumen 12-5, bone pitch 2-5, rosin 2-5, linseed oil 45, turpentine 30, flattening 39.

Attempts have been made to introduce aniline blacks in place of the pitch, in order to obtain a more intense black, but the addition results in the reduction of the drying power of the film.

* The term Japan, as applied to substances which promote the drying of a paint film, denotes generally liquids which dry to a hard film possessing considerable coherence (cf. Japan Drier). Japan driers give a harder film than the oleo-driers, which are elastic and of a drying-oil character, whilst japan driers are of the nature of a resin varnish containing resins or rosin with lead and manganese.

Some japans consist of bitumen with boiled oil and thinners, so that there is a gradation from the coachbuilder's black japan to the ordinary Brunswick black used for grates and iron work. The introduction of Prussian-blue into the boiled linseed oil is said to give a fine black japan of good hardness. Coffignier gives the following formula :

Judea bitumen, 19 ; Madagascar resin, 12 ; boiled linseed oil, 30 ; and turpentine, 39 per cent.

Air-drying Black Enamels. These are made on a similar plan to the coachmakers' black japans, but consist of material which is not so carefully selected, *e.g.* asphaltum, rosin, boiled oil, and petroleum thinners. Some contain only pitch, boiled oil, and turpentine, and are merely Brunswick blacks, for which the following formula may be considered as fairly representative :

45 lb. pitch, 6 galls. boiled oil, and 6 lb. litharge, boiled until stringy and then cooled and thinned with 25 gallons of turpentine.

Another formula may be given, *viz.* :

Gilsonite 32 lb., boiled oil 14 galls., and turpentine 54 galls.

A black for iron work is compounded on somewhat similar lines, *i.e.* :

Asphaltum 48 lb., boiled oil 10 galls., and 8 lb. dark copal gum in 2 galls. of hot linseed oil. As driers, 7 lb. of red lead, 7 lb. of litharge, and 3 lb. of white copperas are incorporated in the melted mixture, which, when cooled, is thinned with 30 gallons of turpentine. A certain amount of coal-tar pitch can be incorporated with asphaltum to give air-drying black varnishes in which turpentine and petroleum are used as thinners.

A quick air-drying black varnish suitable for all kinds of iron work can be made by melting 28 lb. of coal-tar pitch with 28 lb. of asphaltum and boiling for eight hours, with subsequent addition of 8 galls. of boiled oil which is incorporated by heat. After the addition of 10 lb. of litharge and 10 lb. of red lead the mixture is boiled until the mass will set hard between the fingers, and after cooling is thinned with 20 gallons of turpentine. The varnish will dry in one to two hours. The addition of a small quantity of coal-tar spirit (phenol and its homologues) will improve the solubility of the components of black varnishes, but it reduces the air-drying power and is generally restricted to stoving black enamels.

It is evident that the varieties of blacks will be large in number and have special names according to their requirements. They may be bright or dead : *e.g.* Berlin black used for grates and fenders, in which the introduction of a black pigment such as carbon black produces the matt appearance. Coach- and motor-builders require a black japan of first quality for mud-guards, etc., a quick black for iron work drying in about an hour, a black petrol-resisting varnish of brilliant lustre, dust dry in one hour and hardening in two to four hours, used for touching up, and a dead black metal priming capable of standing a great heat for cylinders and motor cars.

Reference to British and American specifications will give some idea as to the requirements to be fulfilled by certain air-drying black enamels.

BRITISH STANDARD SPECIFICATION FOR AIRCRAFT MATERIAL

Bituminous Paint (2 X. 9, 1920).—The paint shall consist of a solution of high-grade bitumen, and in addition to satisfying clauses of this specification shall comply with the special requirements of Appendix 1 (Special test for bituminous paint: Two coats of the paint shall be applied to a wooden panel and, after remaining sixteen hours in bright daylight, a coat of Tung Oil Graphite Paint shall be applied. The film of paint shall become dry after not more than eight hours, and shall adhere to the bituminous undercoating).

Consistency.—The paint shall be of such consistency as will allow of easy application with a brush or spray.

Rate of Drying.—The paint, when applied to wood, shall dry in not more than six hours at a temperature of 70° F. to a glossy, smooth, hard surface, which does not become soft or tacky when the temperature is raised to 100° F.

Elasticity.—The paint, when applied to a strip of thin plate (about 0.036 in. thick) and allowed to dry for twenty-four hours at 70° F., shall show no signs of cracking when the tin is bent round a $\frac{1}{4}$ -in. rod through 180° and straightened out again.

It is evident that this paint belongs to the categories of Brunswick black or iron-work black previously described.

Air-drying Black Enamel (2 X. 10, 1920).—(Note.—This material is to be used only for touching up metal parts.)

Description.—The enamel shall be suitable for direct application by brush or spray. A single coat shall produce a complete covering.

Rate of Drying.—The enamel, when applied to a metal surface, shall dry at 70° F. (21° C.) in not more than eight hours to a smooth glossy film.

Elasticity and Adhesion.—The film of the enamel shall be tested for elasticity and adhesion as follows:

The enamel shall be applied to a panel of 30 S.W.G. tinned iron and allowed to dry in a nearly vertical position for forty-eight hours at 70° F. (21° C.). The panel shall be bent rapidly double over a $\frac{1}{4}$ -in. diameter rod and straightened out again. The enamel film shall show no signs of cracking at the point of bending and shall adhere to the metal surface.

It is evident that the air-drying black enamel is more elastic than the undercoating bituminous paint, and contains a larger percentage of oil, and consequently is slower drying.

An American specification⁷ for an asphalt varnish is more detailed and stringent:

The varnish shall be composed of a high grade of asphalt fluxed and blended with properly treated drying oils and thinned to the proper consistency with a volatile solvent. It must be resistant to air, light, lubricating oil, water, and mineral acids of

the concentration hereinafter specified, and must meet the following requirements :

Appearance.—Smooth and homogeneous ; no livering or stringiness.

Colour.—Jet black.

Flash Point (closed-cup).—Not below 30° C. (86° F.).

Action with Linseed Oil.—Varnish must mix freely to a homogeneous mixture with an equal volume of raw linseed oil.

Insoluble in Carbon Bisulphide.—Not more than 1 per cent.

Non-volatile Matter.—Not less than 40 per cent by weight.

Fatty Matter.—Not less than 20 per cent of the non-volatile. Must be liquid and not show any rosin by the Liebermann-Storch test.

Set to Touch.—Within five hours.

Dry Hard and Tough.—Within twenty-four hours.

Toughness.—Film on metal must withstand rapid bending over a rod 3 mm. ($\frac{1}{8}$ in.) in diameter.

Working Properties.—Varnish must have good brushing, flowing, covering, and levelling properties.

Resistance to Water.—Dried film must withstand cold water for eighteen hours.

Resistance to Oil.—Dried film must withstand lubricating oil for six hours.

Resistance to Mineral Acids.—Dried film must withstand action of the following acids for six hours : Sulphuric acid, s.g. 1.3 (about 40 per cent) ; nitric acid, s.g. 1.22 (about 35 per cent) ; hydrochloric acid, s.g. 1.09 (about 18 per cent).

For the details as to carrying out these tests reference must be made to the specification quoted.

It is evident that the percentage of thinners must not be greater than 60 per cent by weight and the percentage of oil not less than 20 per cent of the non-volatile matter.

It would appear that the specification corresponds with that of an air-drying black enamel.

Black Stoving Enamels.—Black stoving enamels are of great variety, and a similar classification holds, as in the case of resin-oil varnishes, as to elasticity, body or viscosity, and temperature of stoving. One-coating, undercoating and finishing, brushing, dipping, and spraying modifications are in use. The marked difference between clear varnishes and black stoving enamels lies in the presence of bitumen, which may be considered as a neutral resin, and of carbon black, the effect of which is to retard the drying and to modify the viscosity of the mixing. The remaining components will be drying oils with their attendant driers and thinners, chiefly kerosene, since the temperature of stoving is higher than that of resin-oil varnishes, viz. 150°-177° C. Some black stoving enamels contain no resin or rosin, but generally a certain proportion is present, although it is difficult to identify the resins in the presence of a mixture of bitumens, especially if stearine pitches have been used.

In selecting the thinners it must be remembered that the less volatile part must be a satisfactory solvent for the bitumen oil residue at the temperature of stoving. Small amounts of turpentine or coal-tar spirit are often added to ensure complete solution of all the components. Flow and surface are important properties. The finishing coat must have a high lustre and hardness and should show no runs or rivelling at the edges under the conditions of application, dipping, brushing, or spraying. The production of high-quality coatings demands careful selection of the components and of their proportions in the mixing. If an undercoating is used, it must be adherent to the surface and be a rust preventative, providing also a grip for the finishing coat. It will possess small elasticity and great hardness, good hiding power, but no lustre. The undercoating may contain a pigment such as carbon black instead of bitumen, and its function is to leave a dull uniform flattened surface which will fix the finishing coat. Occasionally the metal may be treated with an anti-rust preparation or subjected to an anti-rust process (Coslet process) previous to the application of the stoving enamel. The metal surface must be properly cleaned before application of the undercoat, and if alkaline salts are used these must be thoroughly washed out; if a trace is left on the metal the subsequent saponifying action on the varnish coat destroys the adherence, and the film or films are so seriously weakened that they are easily detached. The general defects will be those of oil varnishes, which will be discussed in a later chapter.

The composition and mode of preparation are based on the incorporation of sweated asphaltum and rosin or a resin with linseed oil (thickened or polymerised) with a thinner, *e.g.* 100 lb. asphaltum, 25 lb. rosin incorporated with 500 lb. boiled linseed oil, or 100 lb. copal run with 50 lb. boiled linseed oil with a solution of 6 lb. of india-rubber in 200 lb. turpentine or petroleum, to which are added 100 lb. asphaltum, incorporated separately with 150-200 lb. boiled linseed oil, and thinned with 400-500 lb. turpentine. The mixture is stated to give an elastic black japan. Again, a mixing suitable for cycles or sewing-machines is said to be obtained by heating together 25 lb. raw linseed oil with 3 lb. Prussian blue (for hardening purposes) and $1\frac{1}{2}$ lb. litharge, until the mass is a thick syrup. It is then incorporated with 5 lb. of a resin and 18 lb. asphaltum, and the whole thinned with turpentine. Another published formula is as follows: 50 lb. hard copal incorporated with 41 lb. boiled linseed oil (lead acetate and white copperas driers), mixed with 200 lb. fused American asphaltum, and the whole boiled until the mass shreds. The mass is thinned to the required consistency.

It is evident from the above formulæ that the principles involved do not differ from those described under resin-oil varnishes, except in the length of time of heating to produce the desired viscosity. The proportions of the components will depend on the requirements and on the temperature of stoving. N. C. Jensen⁸ claims to furnish metals with a protective adherent film by the

application of oil at a high temperature, the film acting as a protection against rust and also as an insulator. The use of petroleum or non-aqueous thinners has been challenged, and the British Thomson Houston Co.⁹ claim that a black japan can be made with water thinners by incorporating 5 galls. japan base (asphaltic material and a drying oil) with 10 galls. water containing $\frac{1}{2}$ gall. ammonia (s.g. 0.9) and 10-20 per cent by volume of a 20 per cent solution of glue. This departure on the lines of a water paint is worthy of careful consideration. Another proposal is to prepare an emulsion of an asphalt oil base in water and to deposit this base on the metal by means of an electric potential-difference maintained in the bath containing the emulsion; the object to be coated is made the anode. The metal must be pre-heated, in the case of large articles, before being dipped into the tank. Since the japan is deposited free from solvent, there is no resultant drip when the work is conveyed to the baking ovens.¹⁰

The application of stoving black enamel has already been discussed under varnishes. The resisting power of the stoving enamels will depend essentially on the stability of the binding material, and, if on an oil basis, on the nature and proportion of the oil. Generally, stoving black enamels are more resistant at the ordinary temperature to the action of alkalies than resin oil varnishes. The sluice gates on the river Nile are examples of a structure which is subject to attack by alkaline salts present in the river water at certain times of the year. Bitumen sufficient to protect the oils and resins used on the sluice gates forms the base of the coatings, and the colour can be modified by the use of strong staining pigments.

Black Leather Varnishes.—Varnishes on an oil basis have been largely used for patent kid leather, although they have been partially replaced by nitrocellulose mixings. The prepared leather is first coated with "daub," which is of the nature of a preparing coat for covering the grain surface of the leather with an impermeable finish through which the finishing coats will not permeate. A special lead-drying oil containing (per gallon of oil) 0.3 lb. litharge, 0.1 lb. manganese borate, 0.6 oz. burnt umber, and 0.1 lb. Prussian blue is prepared. It is essential that the ingredients should be in as fine a state of subdivision as possible before addition to the oil. The mixture is boiled at 500° F. and kept at that temperature for six to eight hours until a thin jelly is obtained, allowed to cool, and the temperature raised to 500°-550° F. for a further period of four to six hours. The film must dry in twenty-four hours; if it does not, the boiling must be continued for five to six hours at 500° F. The temperature is allowed to fall slowly to 100° F., and the jelly is then thinned with petroleum spirit in the proportions of 3 galls. to 10 galls. of oil, so as to produce a thick viscous mixing. The mixture is applied slightly warm with a wooden slicker in a japanning stove at 95°-100° F. and carefully spread over the grain surface of the leather, the excess being scraped off. After the application of the first coating, the skins are placed in

the japanning stove until the coating is quite dry, when they are removed and exposed to sunlight and air for twenty-four hours. Some manufacturers use a mixture of soluble nitro-cotton, dissolved in amyl acetate, for the "daub," instead of the linseed oil coating. The strength of the soluble cotton mixture is about 3 per cent. It must not be too thin, otherwise it will penetrate into the leather and make it too hard. It is best applied with a varnish brush, the leather being given a good coating and then dried preparatory to applying the black varnish.

The first varnish is made on the lines of the "daub" and may consist of 10 galls. linseed oil, 5 lb. Prussian blue, and 3-4 lb. vegetable black. The oil is boiled twelve hours at a temperature of 600° F. and the vegetable black must not be added until the completion of the oil boiling process; moreover, the oil should not be boiled for more than one hour after making the addition of the vegetable black. After the application of the "daub" the surface is pumiced and all dust is brushed off. The first coat is applied with a brush. After application of the first coat of varnish, the leather is returned to the japanning stove and dried ready for the finishing coat. For the finishing coat 10 galls. linseed oil, 2 lb. Chinese blue, and 2 lb. manganese borate are boiled at 650°-680° F. for twelve hours. The finishing varnish is applied after pumicing the skins, and in as thin and level a film as possible. After the application of the finishing coat, the leather is returned to the japanning stove and stoved for at least twenty-four hours until quite dry. It is advisable to expose the finished leather for at least two days to air and sunshine so as to make the enamel more elastic.¹⁴

In France the requirements for patent leather varnishes are elasticity, a certain amount of resistance after drying, and absence of stickiness. The film produced must not crack on exposure to the cold or by long usage. The linseed oil used must be "tanked" oil and free from mucilage. The following formulæ are given for varnishes for high-class shoes: (1) 100 litres of linseed oil are slowly heated to 200° C., when 100 grams litharge are introduced, and the temperature maintained for twenty-four hours. One hundred grams Prussian blue, 650 grams manganese borate, 250 grams manganese carbonate, and 50 grams talc are added with constant stirring and the temperature raised to 250° C. Continued stirring is essential, and heating is maintained the following day, when frequent tests are made by "spotting" the varnish on a cold glass plate. When a test shows that it has thickened sufficiently, it is heated for a further quarter of an hour and allowed to cool. Fifty to sixty kilos. of turpentine previously warmed to 50°-60° C. are added. The varnish is stored out of contact with air. (2) For use, 6 kilos. of the varnish are worked up with 250 grams lamp-black and the necessary quantity of turpentine added to give a workable consistency. This corresponds to the English "daub."

Another varnish is made by heating 100 kilos. linseed oil at 220° C. with 300 grams litharge for one or two days, and the

following substances are added in the order named: 2 kilos. lead acetate, 1 kilo. manganese borate, $\frac{1}{2}$ kilo. manganese oleate, and 4 kilos. lampblack. The temperature is then raised to 250°-260° C., and heating continued until the mass has a tarry consistency and sets when a little is dropped on a glass plate. When required for use, 50 kilos. are diluted with 80 kilos. of turpentine, and 2½ kilos. of lampblack added. This is passed through a mixer several times and finally strained. (3) An oil for surface varnishing is made by heating 45.3 kilos. linseed oil with 100 grams of litharge for two days at 200° C., adding 1.36 kilos. Prussian blue, 0.45 kilos. Syrian asphalt, 0.45 kilos. of manganese carbonate, and 50 grams verdigris. The temperature is raised at first to 280° C. and finally to 300° C. When, by the usual test on glass, it is found that the heating is sufficient, the mass is cooled to 80°-100° C. and 100 litres of turpentine are added.

For varnishes for furniture leather, the first and second coats are prepared on the same basis. For colouring, such pigments as ochres, siennas, and Prussian blue are used, also aniline colour-lakes precipitated on kaolin or similar bases.

It will be seen that the French formulæ do not differ in principle from the English. The method is to produce a polymerised lead-drying oil which is hardened by the iron of the Prussian blue. Chinese blue causes less waste than Prussian and is more easily incorporated.¹¹

Varnishes containing Wood Oil.—In view of the functions of the oil constituent in varnish, it is not surprising that attention has been directed to the substitution of linseed oil by China wood oil. The greater facility with which a high degree of viscosity can be obtained by heat treatment and the greater concentration of glyceride having an affinity for oxygen are properties which indicate the suitability of China wood oil as a constituent of varnish. Whilst a film of polymerised linseed oil never attains a degree of hardness suitable as a protective layer to withstand a reasonable degree of abrasion and requires the presence of hard gum resin, the oxidation product of polymerised China wood oil yields a film which compares favourably with that of copal linseed oil varnishes; moreover, it possesses a lower degree of susceptibility to cracking at low temperatures. The great difficulty of controlling the thickening of the oil militates considerably against its use as the sole constituent of a varnish; in addition, the film acquires a matt surface on drying which is undesirable. Incorporation with gum resins is a matter of extreme difficulty owing to the high temperatures to which the oil is subjected, coagulation usually resulting. In view, however, of the remarks above as to the intrinsic hardness of the oxidised China

* Wood oil acids prepared from China wood oil may be heated above 280° C. without coagulation. If wood oil acids be used the hardest copals, e.g. Zanzibar and Angola, can be dissolved in a powdered "unrun" condition at a temperature above 280° C. to give a clear liquid which can be mixed with linseed or other drying oils and thinned with turpentine, etc., to give good air-drying coatings.

wood oil, the necessity for the introduction of a hard resin is not so urgent, and in order to increase the hardness of the oil film and to reduce the tendency of coagulation of the oil during heat treatment, advantage may be taken of the lower temperature of incorporation required for a soft resin. Reference has been made in an earlier chapter to processes for the thickening of China wood oil without gelatinisation. The most successful is the addition of common rosin to tung oil, which allows of the desired degree of polymerisation being obtained without danger of coagulation.

Several advantages are gained by such admixture; the undue rapidity of "setting," as distinct from the attainment of the maximum increase in weight, is diminished, and the liability which a varnish made from tung oil shows to form wrinkles or "webbing" during drying is overcome. Many variations in product are possible by employing different proportions of rosin and oil, and differences of behaviour during drying may be obtained by varying the nature and proportion of drier, etc. It is a significant fact that, in spite of the prejudice which the consumer has had hitherto, in regard to varnishes containing rosin as their sole gum constituent, varnishes of this class were found by actual trial over long periods to be the only ones satisfactory for the protection of "doped" fabrics or aircraft. Varnishes on a basis of tung oil and rosin are now in comparatively large demand, especially where the varnish film comes in contact with water, because the emulsion referred to in the previous chapter is not manifested unless the amount of metallic base in the mixing is excessive.

A method of preparing such wood oil varnishes consists in heating rosin or a suitable acid resin and tung oil together, with the addition of lime and driers. Addition of linseed oil or linseed oil acids allows of longer heating on the fire; 10 parts of linseed oil with 2 parts of wood oil heated at 280° - 290° C. for five to six hours gives a heavy-bodied oil suitable as a light-coloured vehicle for white enamels (interior or exterior). Addition of lime causes whitening when the varnish film is immersed in water. To overcome this "chalking," the rosin may be hardened by esterification with glycerine and by blowing air through the melted ester (*vide* ester gums). The webbing or frosting effect is evident in all tung oil varnishes, even if they contain as much as 20-30 per cent of linseed oil. This defect is the result of insufficient heating of the mixture on the fire, *i.e.* inadequate polymerisation previous to the addition of thinners.

Another method of transforming China wood oil into a non-gelatinising modification is to allow the oil to flow in a fine stream through a slightly inclined tube, which is kept at the necessary temperature by means of an air or metal bath. The colour of the changed oil is equal to that of the original; it dries hard and lustrous, and contains no resins. The oil can be thinned with turpentine, white spirit, etc. With linseed oil and with stand oil it furnishes hard and glossy varnishes.¹²

It must be pointed out that wood oil under certain conditions

TYPES OF OIL VARNISHES

can be heated up to 320° C. and kept at that temperature for over an hour without gelatinisation. Great thickening occurs, but without loss of solubility in ordinary solvents: The acidity of the oil increases from between 5 and 6 to 19-21 and the iodine value falls from 165 to 94-103. The disadvantage of this modification of wood oil is that it does not yield a hard dry film, and the tack caused by the presence of some unknown substance restricts its use. It does not "web" as in the case of partially cooked wood oil.

M. Toch, in a paper read before the American Chemical Engineers at Savannah, states that up to 1914 there was hardly a paint or varnish specification which did not prohibit the use of rosin, because of its various undesirable characteristics, rendering it unfit for high-class paints and varnishes. The advent of China wood oil has now made rosin a legitimate material in paint and varnish manufacture, and has removed the objection to it on the grounds of friability, high acidity, tendency to become soft and sticky in damp weather, to change colour, and to form resinates. When heated in correct proportion with rosin which has been partially or wholly converted into resinates of lead or similar compounds, China wood oil can be heated to 315° C. without danger of solidification, and a varnish is obtained which, although of a fairly high acid value, possesses more remarkable qualities than the best kauri linseed oil varnish ever made. The gloss and hardness of wood oil rosin paints, compared with linseed oil paints after a three years' exposure on the Atlantic coast, were equally good and the tung oil paint gives a better surface for re-painting. The demand for rosin in tung oil varnishes has raised its price from two cents a lb. to ten cents a lb.; possibly it may in the future become dearer than copal resins.¹³

Sabin¹⁴ states that wood oil varnishes are less durable than oleo-resinous varnishes of the older type; their hardness, brilliancy, and remarkable quick-drying qualities ensure their general use, but where extreme durability is required or where the finished surface is to be re-varnished when it becomes dull, their use may not prove to be economical or satisfactory.* The general opinion on the matter of the durability of wood oil varnishes is in favour of Toch's experience, provided that proper precautions are taken in the manufacture.

The disadvantages attendant on the acidity of rosin with regard to the use of these varnishes as "mixing" varnishes, i.e. those intended for use with basic pigments, are overcome by substitution of the acid rosin by "hardened rosin" (alkaline earth resinates) or "ester gum" (glycerine rosin ester). A typical formula for a rosin wood oil varnish with a high rosin content is: rosin, 28.5; linseed oil, 17.0; China wood oil, 11.5; lead linoleate, 1.0; manganese resinate, 2.5; and turpentine, 43 per cent.

* It must be pointed out that although a rosin-wood-oil film retains its lustre on exposure the surface shows a network of fine cracks, whereas a resin-linseed-oil film will have become rough and uniformly dull.

The production of rosin esters and their incorporation with wood oil has already been referred to under Ester Gums.

There are several drawbacks in the use of these varnishes for inside work, because they are apt to bloom unless special precautions are taken in their manufacture. The rapid setting as well as the polymerisation of the wood oil are conducive to bloom. If the resin content is high, they are liable to crack on exposure to the weather, but they retain their lustre well. Some rosin wood oil varnishes "chalk" in water, indicating that the latter has penetrated and become emulsified in the film; this fault, in itself, is not very serious. The emulsification is accelerated by the presence of the lime, used to harden the rosin, and of linseed oil.

The proportion of rosin to wood oil must be carefully chosen, since it has been shown that excess of wood oil or of rosin are both undesirable. A wood oil floor varnish may be obtained by heating a mixture of 10 kilos. rosin and 5 kilos. wood oil to 310°C . The mixing can be worked up with any pigment, even lead or zinc whites, without thickening. Andés (*loc. cit.*) gives the following formula for a wood oil floor varnish: 100 kilos. rosin, 4 kilos. litharge, 1 kilo. hydrated oxide of manganese, and 1 kilo. zinc white are heated at 260°C . until the metallic oxides are dissolved. Fifty kilos. of wood oil are added and the mixture heated to 305°C . It is then removed from the fire and cooled to 250°C . and 30 kilos. of wood oil are added. The temperature is raised to 280°C . and maintained for one hour. After allowing it to cool to 240°C ., it may be diluted with turpentine or a suitable thinner. Zinc white is said to be superior to lime for the hardening of the rosin.

Paracumarone Oil Varnishes.—Reference has been made in the chapter on resins to the properties of the polymerides of paracumarone and para-indene. The technical resins are neutral bodies, insoluble in alkalies, unattacked by acids, ammonia, and soaps, and insoluble in alcohol. Paracumarone resin when properly prepared is a brittle, amorphous, rosin-like material. The poorer grades are black, but those used in varnishes vary in colour from reddish brown (grade E. rosin to W.W. rosin), and are transparent. The grades melting above 125°C . are used, because the more fusible varieties give tacky films. King, Bayard, and Rhodes¹⁵ describe the manufacture and properties of oil varnishes made on a paracumarone basis.

China wood oil containing 15 per cent of linseed oil is incorporated with the resin in the proportions of 5-40 galls. per 100 lb. resin. The driers used are cobalt or manganese linoleates (1.5 lb. cobalt linoleate per 100 lb. of oil). The thinner is a heavy refined coal-tar naphtha, distilling above 160°C . The resin and oil are heated together to 290° - 300°C . at the rate of 2.5°C . per minute (the temperature of incorporation is higher with increasing hardness of the resin). The mixture is allowed to cool, the thinner added, and subsequently the drier solution is added below 100°C . The drier solution is prepared by heating 100 parts of cobalt linoleate with 84.2 parts of linseed oil for two hours at 200°C ., 42.1 parts tung oil are added

and the heating continued at 200° C. for one hour. After cooling to 160° C. the mixture is poured into 600 parts of the coal-tar naphtha thinner. The varnishes are clear and paler than ordinary oil varnishes; they set in three hours and dry hard in twenty hours, giving films which are smooth and brilliant in lustre. The rubbing tests on wood panels are quite satisfactory. The varnish films when tested for water-resistance by the U.S. Railroad Administration Specifications for Spar Varnish (1/5/18) showed no whitening. The weathering tests gave satisfactory results. Paracumarone varnishes are stated by the authors to be superior to resin oil varnishes. The advantages of the presence of a neutral resin incorporated with wood oil are self-evident, but there was a disadvantage in the thinners being restricted to those essentially on a coal-tar basis.

More recent investigations have shown that linseed, soya, menhaden, perilla, cotton seed, and a few other drying and semi-drying oils may be used. Cumar gum is entirely soluble in all these oils. Various types of thinners, including turpentine, wood spirits, and petroleum, have been found suitable. Alcohol is not satisfactory, as it is not a solvent for the resin. If lead be used as a drier, it must be in the form of a clear liquid drier to be added after the heat treatment.

Three types of varnishes may be quoted:

Spar or Long-oil Varnish—100 lb. cumar; 20 lb. rosin; 75 lb. linseed oil; 150 lb. tung oil; 380 lb. thinner; and 2½ lb. cobalt linoleate (solid). The tung oil and rosin are heated to 280° C. and drawn off the fire. When the mixture "strings," the linseed oil is added to chill, then the cumar is added and the mixture heated to about 510° F. for fifteen to thirty minutes, cooled, the drier added, and then thinned.

Short-oil or Rubbing Varnish—100 lb. cumar; 94 lb. tung oil; 14 oz. cobalt linoleate (solid); and 205 lb. thinner. The tung oil is heated to 470° F. and 75 lb. cumar added with stirring while on the fire. The temperature is run up to about 277° C.; the pot is withdrawn and held until a drop on cold glass sets in a hard button. The balance (25 lb.) of the resin is added with stirring to check the heat. It is important to obtain the proper body without "stringing." The drier and thinner are added as in the previous case.

In view of its lower acidity cumar resin does not retard the gelation of tung oil as effectively as rosin.

J. M. Kessler¹⁶ claims to prepare a lacquer by incorporating tung oil with twice its weight of cumarone resin (m.p. above 85° C.) and dissolving in toluene, benzol, xylenes or a similar solvent.

Cumar Varnishes will mix readily with other oil varnishes, and as they contain no acid resin, they are useful in preventing "livering" with lead and zinc pigments, in paints, enamels, etc. The resin may be used as a binder for oil stains and in printing inks. The lower melting point grades (m.p. 50°-70° C.) are used in cheap inks to body oils.¹⁷

Slushing Oils.—It is often desirable to protect temporarily bright metal work either during storage or transit. P. H. Walker and L. Steele¹⁸ state that the materials shall adhere to the metal surfaces at the ordinary temperature and shall remain permanently in such a condition that they may be removed readily by cotton waste wetted with kerosene. On polished steel brasses and copper surfaces below 100° F. there shall be no stain or other evidence of corrosion within five days. A salt spray test is specified, and, when time permits, plates covered with the material should be exposed to the weather for not less than sixty days with no appreciable rust formation. A formula is put forward comprising the use of rosin and wax with solid petroleum jelly: 5 parts Candelilla wax, 6 parts H. rosin, and 50 parts petrolatum, U.S.P., or 2 parts Carnauba wax, 5 parts H. rosin, and 50 parts petrolatum, U.S.P. A more fluid preparation may be obtained by the use of a liquid kerosene. The so-called slushing oils are made on the basis of the above formulæ.

If timber has to be temporarily protected, the parts, which are eventually to be glued, should be first coated with a thin glue size prepared from an approved glue size and of a concentration approximately half that normally employed for glueing. The part should be allowed to dry for not less than twenty-four hours, and then be completely covered with one coat of shellac varnish, both sized and unsized portions being thus treated. When the parts are to be assembled, the varnish layer should be completely removed (by scraping) from those portions which have been sized and are to form the faces of a glued joint. After assembly the protective treatment, as detailed under the Protection of Timber, should be employed.¹⁹

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CHAPTER XIV

PROPERTIES AND DEFECTS OF VARNISHES

The Viscosity of Varnishes. In the consideration of the flow of a varnish, viscosity is of the highest importance. Consistency determinations of varnishes are invariably made to ensure a uniform product. Viscosity of a fluid is the property to which is due the internal resistance offered to its motion at any point with a velocity different from that at an immediately adjacent point. Different fluids vary greatly in the rate and ease with which they flow. Although specific gravity may have an important influence on the rate of flow, it is not the determining factor. The term "body" is often used to indicate both resistance to flow and the quantity of solid matter. To obtain a definite expression for the viscosity of a fluid, it is necessary to consider a stream in which the velocities of the liquid in adjacent parallel planes are in parallel directions and increase uniformly with the distance apart of the planes. Under these circumstances any one plane in the fluid will exert a force upon any other plane; the magnitude of the force will depend upon the area of the planes and upon their distances apart, while its direction will be in the direction of flow of the stream in the case of the slower moving plane, and counter to the flow in the case of the faster: *i.e.* it will be tangential to either of the planes considered. Expressing these statements in the form of an equation, if F be the tangential force or drag experienced by one of the planes of area, V the difference between the velocities of the two planes, and L be the distance between them, granting that V is proportional to L , then

$$F/A = -\eta \frac{V}{L},$$

where η is a "coefficient," the value of which depends only on the particular liquid between the planes and on the system of units employed. The minus sign in the above equation is to indicate that the force of drag is in a direction tending to make the velocities of the two planes equal. The numerical value of the coefficient is called the viscosity of the liquid. The "dimensions" of η are $ML^{-1}T^{-1}$. The coefficient of viscosity of a fluid is the numerical value of the tangential force on unit area of either of two parallel

planes at unit distance apart, one of the planes moving with unit velocity in its own plane relatively to the other, the space between these planes being filled with the viscous substance.

A distinction must be made between the values of viscosity expressed in absolute units as above and "viscosity numbers" used in industrial work, which are derived from a comparison of times of outflow of the fluid under consideration with the corresponding time for some substance arbitrarily chosen as a standard, e.g. water, rape oil, or glycerine; such values are independent of any scale of units, and are not necessarily ratios of true viscosities. In some cases the actual time of outflow of a certain quantity of liquid from a specified type of apparatus is spoken of as the "viscosity" of the liquid, which must be regarded as unsatisfactory because of the difficulty of correlating results expressed in this way with the values obtained by other methods or even other apparatus of a similar type. It is true that the standard sample method of comparison is the most generally used, especially in control of the uniformity of the product. Nevertheless it is of advantage to select methods in which the viscosity values are capable of being expressed in the metric system of units (centimetre-gram-second). The term "poise" has been selected for the unit of viscosity on the metric system, i.e. dynes per sq. cm. per velocity gradient per cm. of 1 cm. per second. The unit is named after Poiseuille, and the suggestion, originally due to Deeley and Parr, has been adopted by the Bureau of Standards, U.S.A. For liquids of low viscosity the unit "centipoise" (0.01 poise) is convenient. The viscosity of water at 20° C. is nearly 1 centipoise, so that the viscosity number of a liquid based upon a comparison with water at 20° C. is equal to the true viscosity of the liquid in centipoises.

Types of Viscometers.—The methods used for the determination or comparison of viscosity are many and varied. There are four types of viscometers in general use: (1) Air Bubble; (2) Falling Sphere; (3) Torsion (rotating disc or cylinder); and (4) Efflux (capillary tube).

(1) *Air Bubble Type.*—Small tubes of approximately equal size and diameter are used. The tube is filled with liquid to a mark, and a cork inserted so as to leave a small intervening air space. A tube containing a sample of the desired consistency is used as a standard. When a test is made, the air space in the sample to be tested should be of approximately the same size as that in the standard. The tubes are quickly inverted and the time required for the air bubbles to rise to the top or to a certain mark in the tube is noted. The test indicates roughly whether a given lot of material has the same viscosity as that of the selected standard. It is sufficiently accurate for controlling the consistency of varnishes made in the factory.

(2) *The Falling Sphere Type.*—Viscosity is sometimes measured by dropping a steel ball in a vessel containing the fluid and timing the fall between two marked points. The method gives an accurate

measure of viscosity for very viscous liquids. The velocity of a sphere falling vertically in a fluid in relation to viscosity was investigated mathematically by Stokes, who derived the well-known equation

$$V = \frac{2}{9} \frac{g r^2 (s - \sigma)}{\eta},$$

where V is the velocity of the sphere, r the radius and s the density of the sphere, σ the density and η the viscosity of the liquid. Stokes' equation applies only to a sphere falling through an infinite extent of liquid, but the velocity of a small sphere falling axially through a viscous liquid in a cylinder has been discussed mathematically by Ladenburg and Lord Rayleigh. Allen and Ladenburg made use of the principle for the determination of the viscosity of Venice turpentine under pressure. Sheppard¹ has used the method of the falling sphere for the determination of the absolute viscosity of viscous liquids, *e.g.* solutions of nitrocellulose, but the correction formula for the effect of the walls of the vessel on the time of fall of the ball is not that obtained mathematically by Ladenburg, Rayleigh, and Allen. Gibson and Jacobs² have applied the correction laid down by the three former investigators, and find that, if spheres be used in tubes of the same dimensions, the only variables are relative density, viscosity of the liquid, and time of fall. A simple equation,

$$\frac{\eta}{\eta_1} = \frac{(s - \sigma) T}{(s - \sigma_1) T_1},$$

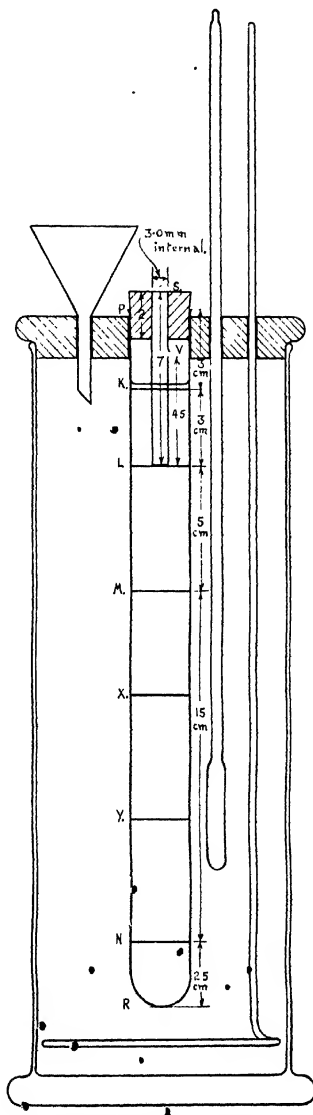


FIG. 32.—Falling sphere viscometer.

T and T_1 = time of fall of the sphere through a length s ,
 σ and σ_1 are the densities of the liquids,
 η and η_1 = the viscosities of the two liquids,

s obtained resembling the expression used for the efflux pattern of a capillary viscometer. The method can then be employed to obtain the viscosity of a liquid when the time of fall for another liquid of known viscosity is known. Fig. 32 shows the form of apparatus used in the method. For the experimental details reference must be made to Gibson and Jacobs' paper and to the British standard methods for the determination of viscosity in absolute units (B. Eng. Stand. Assoc., 1923). The method is suitable for liquids the absolute viscosity of which is not less than 10 poises. For liquids of lower viscosity than 10 poises the method is not suitable, owing to the smallness of the sphere required. It is also unsuitable for deeply coloured liquids in which the sphere cannot be clearly observed. A modified form has been suggested by J. E. Ramsbottom³ which is applicable for the determination of the viscosity of opaque liquids and for liquids with viscosity in poises as low as 0.33. The sphere used is a steel ball half an inch in diameter, provided with a small hook to which is attached a fine thread passing over a special pulley of low friction and connected to a counterpoise. The time of fall of the sphere is indicated by the rise of the counterpoise. The viscosity of such a substance as drawing-ink on the one hand and warm asphaltum on the other can be readily determined. The method is independent of density determinations. With this apparatus the viscosity of opaque liquids over a wide range can be determined by simply altering the weight of the counterpoise. The formula used is

$$\eta = K \cdot \frac{P_1 - P}{R - R_1},$$

where R and R_1 are the rates of fall with counterpoises P and P_1 and K is the constant of the viscometer determined by using a standard liquid. The following table shows the results obtained by the falling sphere method and by Ostwald's capillary tube method:

	Falling Sphere.	Ostwald's Viscometer.
Glycerine at 20° C.	8.5 poises	8.5 poises
Furnace oil	1.11 "	0.92 "
Aluminium dope	8.25 "	8.25 "
Tricresyl phosphate	1.97 "	2.0 "

(3) *Torsion Type*.—In instruments of this type a torsional pendulum is used to measure viscous resistance. They consist essentially of a cup containing the fluid the viscosity of which is to be measured, and a cylinder which is suspended in the fluid. In some viscometers, as in the Doolittle, a cylinder is rotated in the fluid and the viscosity is measured by noting the retarding effect of the fluid. In the MacMichael apparatus the cup containing the fluid is rotated and the viscosity measured by noting the angular

distance through which a disc is carried by the fluid. The Doolittle viscometer determines the retardation of the rotation of the cylinder of standard size immersed in the varnish.

*Doolittle Viscometer.**—The greater the viscosity of the liquid, the greater is its slowing action on the torsion pendulum of the instrument. The specific gravity has no influence on the result. The apparatus consists of a steel cylinder 2 in. high by $1\frac{1}{2}$ in. in diameter, suspended by a steel wire from a fixed point, the wire passing through and firmly attached to a horizontal graduated disc. The cylinder is immersed in a vessel containing the varnish, and this vessel is surrounded by a jacket containing water or other liquid which can be heated to the necessary temperature. The wire is brought to the zero mark on the disc, so that there is no torsion in the wire. The disc is now fixed and the wire turned through a complete circle (360°) and fixed also. When the varnish is at the required temperature the disc is released and the angular oscillation is observed (1) to right, (2) to left, and (3) to right again. The disc is clamped and the wire twisted through 360° in the opposite direction. The disc is again released and three observations of the angular oscillation are taken: e.g. $360^\circ-0^\circ-340^\circ-0^\circ$, 332° in the other direction, $0^\circ-324^\circ$. The first swing is neglected and the readings are taken from 340° onwards. First complete swing: $340^\circ-0^\circ-332^\circ:-672^\circ$. Second complete swing: $332^\circ-0^\circ-324^\circ:-656^\circ$; retardation 16° .

The instrument is well adapted for plant control work, especially in the case of bituminous varnishes. The greatest difficulty is in the interpretation of results obtained by it. It is impossible to standardise the dimensions, and an instrumental unit cannot be derived. The greatest source of error, and one which makes strictly comparative readings impossible, arises from the constantly varying rate of shear to which the liquid is subjected. There is apparently no way of calculating absolute viscosity from the readings. Since the observations are not proportional to viscosity, the use of the instrument for accurate research work is doubtful. It is of value as a control instrument, especially where it is desired to bring a fluid to a standard viscosity. The instrument may be standardised against a solution of cane sugar in water.

MacMichael Torsion Viscometer.—In instruments of the MacMichael and Couette types the liquid is rotated by an electric motor and the viscosity transmits a pull on a cylinder which twists a wire. In the MacMichael instrument a cup, containing the liquid to be tested and in which is suspended a torsional pendulum, is rotated by an electric motor. The pendulum consists of a disc 60 mm. in diameter and 5 mm. thick suspended by means of a fine torsion wire. Different-sized wires can be used for varying degrees of viscosity.† The speed is controlled and varied by means of variable pressure on a disc operated by the motor. For high viscosities heavier wires or slower speeds, or both, must be used.

* Cf. Figs. 33, 34, pp. 74, 75, vol. ii. Fryer and Weston, *Oils, Fats, and Waxes*.

† The torsion wire is firmly fixed in a tube, near the upper end of which is attached a disc divided into 300 equal parts known as MacMichael degrees.

The instrument is applicable over a wide range of viscosity. The readings of the instrument vary directly with the rate of shear. It is especially adapted to varnish control work, where it is frequently desirable to make determinations on unfiltered samples. The actual readings of the instrument have little significance and the dimensions cannot be standardised. The instrument does not give absolute viscosities directly, and, since the standardising of dimensions is impracticable, a unit based on instrumental readings is not possible. The results must be expressed through the medium of some standard testing fluid, of which either the absolute viscosity is known, or which at least always shows the same viscosity under like conditions.⁴

Efflux (Capillary Tube) Methods.—Capillary tube viscometers are of two forms: (a) U-tube viscometers, (b) Co-axial bulb viscometers.

The method of determination depends on the equation of Poiseuille:

$$q = \frac{\pi P R^4}{8 \eta L},$$

where q = volume of liquid flowing in unit time, P = fall in pressure of the liquid over a length L in the capillary tube of internal radius R , η = viscosity of the liquid. No turbulent flow of the liquid is allowed. The Kinematic Viscosity = $\frac{\text{Absolute Viscosity in poises}}{\text{Density in gms. per c.c.}}$.

The capillary should be so selected that the time of flow in any determination is not less than 100 seconds. It is convenient that the length of the capillary, the U-tube viscometer, be about 10 cms., in which case its maximum diameter, which will depend upon the kinematic viscosity of the liquid under observation, should be selected from the data given in the following table:

No.	Kinematic Viscosity.	Maximum Diameter.	No.	Kinematic Viscosity.	Maximum Diameter.
1.	0.009-0.072	0.054 mm.	3.	0.32-2.56	2.79 mm.
2.	0.054-0.43	1.33 „	4.	1.19-15.3	5.3 „

Fig. 33 shows the form of the two varieties of viscometer. The time of flow of the liquid between two marks on the instrument compared with the time of flow of a standard liquid in a tube of the same dimensions, together with the density of the two liquids at the temperature of outflow, will give a value in terms of a standard. If t and t_1 be the times of flow of the varnish and glycerine respectively at 20° C., and d and d_1 be their specific gravities at 20° C., then the viscosity of the varnish is given by

$$\eta = \frac{100td}{t_1d_1}$$

(glycerine = 100 is a convenient practical standard).⁵

In the co-axial bulb viscometer the range is from 0.009 to 15 poises, with internal diameter of capillary from 0.054-0.4 cm. For details as to use see Standard British methods for determination of absolute viscosity (*loc. cit.*)*.

These forms of instrument are most frequently used for clear varnishes.

* Distilled water, 40 or 60 per cent cane-sugar solution, and castor oil are recommended as standard liquids for calibration.

For opaque liquids the Lidstone Viscometer may be used. It consists of a capillary tube through which the sample is drawn by a flow of mercury, the rate of flow being determined by timing the movement of the meniscus between the liquid and mercury instead of, as is usual, that between the liquid and air (*J.S.C.I.*, 1918, 37, 1481).

Other forms of viscometers are those designed by Redwood, Engler, Saybolt, Coleman and Archbutt.⁶ The first three are fully described in many text-books on petroleum, whilst the Coleman-Archbutt differs from them in construction, being made of glass. In principle the four are the same. In the Coleman-Archbutt instrument (Fig. 34) the varnish tube (glass) has graduations marked on it for 10, 25, and 50 c.c.; the tube consists of a glass pipette, which is closed with a plug of soft wood. The jacket, which is of glass, is filled by means of a funnel G and emptied by the tube b. The tube and jet are carefully closed, the jacket is filled with water at the required temperature (20° C. or 40° C.) and kept at that temperature for some time. The varnish at the desired temperature is poured into the efflux tube (closed with a plug) to a point a little above the volume mark and stirred with a thermometer until it is exactly at the required temperature. The number of seconds required for the escaping oil to reach the zero mark is observed with a stop watch. For the determinations at a higher temperature to obtain a ratio number, e.g. viscosity at 20° or 40° C./viscosity at 100° C., the jacket may be heated by steam and

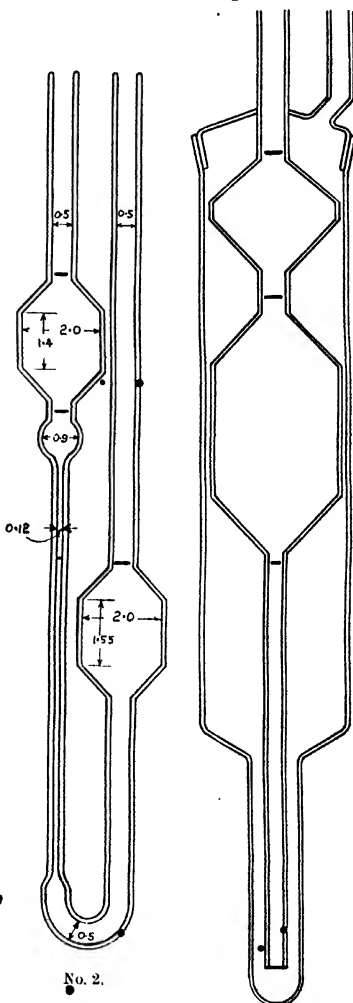


FIG. 33.—Two forms of Ostwald's Viscometer.

the observations conducted as above. The viscometer may be standardised, as in the Redwood instrument.

Seaton, Probeck, and Sawyer⁷ state that varnishes show two types of solution, viz. true and colloidal. They may under certain conditions show the Tyndall effect, *i.e.* a strong opalescence when a beam of light is passed through the varnish, although indi-

vidual particles cannot be distinguished by ultra-microscopic methods. The viscosity-temperature curves of varnishes (determined by the Doolittle method) containing resin-oil (not polymerised) are curves, whilst varnishes containing highly polymerised oils give straight lines. Decrease in dispersion of the components of emulsoid colloids increases the viscosity, and addition of "thinners" lowers the viscosity by increasing the dispersion of the polymerised components. If Seaton's view be correct, the viscosity-temperature curve before further

addition of a solvent to a varnish containing polymerised components would be a straight line, whereas on addition of a solvent thinner a curved line would result. The results of unpublished experiments in the writer's laboratory go to confirm Seaton's conclusions. The relationship may be of importance in detecting the presence

of polymerised oil. Further investigation in this direction is advisable. In many varnishes viscosity changes occur within the first twenty-four hours of manufacture, but they become constant in about a month's time, and unless a constant value be reached within that period the varnish may become unsuitable. The changes during "ageing" are marked in the heavy resin varnishes, because the dispersion of the resin is very sensitive to changes of condition, and especially to changes of acidity. The importance of viscosity measurements in standardisation of aeroplane dope and aircraft varnishes has

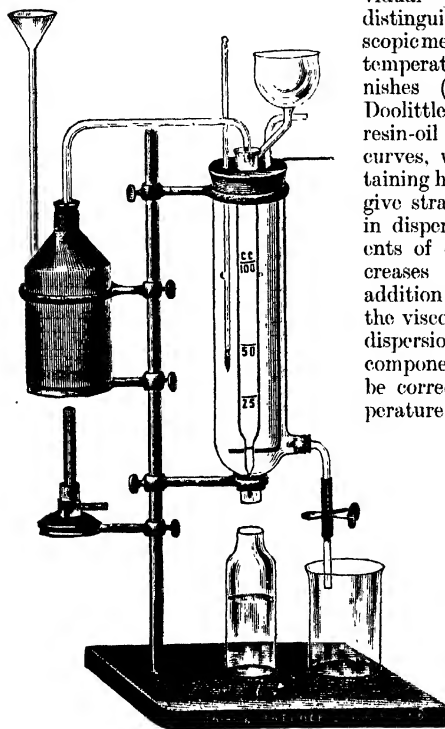


FIG. 34.—Coleman and Archbutt Viscometer.

been recognised as a determining factor in the flow and freedom of working of these coatings. In view of the variety of composition of varnishes, the volatility of the thinner as affecting the flow is of considerable practical importance, because two varnishes having the same viscosity may show different freedom of working due to the inequality in volatility of the thinners, which would be indicated also in the values of the viscosity temperature coefficient. No published observations are available showing the variations in the viscosity with the resin content, although it is admitted that the dispersion of the resin is a dominant factor in the viscosity. Systematic observations on the relationship of resin-oil content to viscosity are much desired. It must be pointed out that the viscosity concentration curve in aqueous emulsoids rises steeply in a curved line, whilst the corresponding graph in varnishes is a straight line. In varnishes with large resin content there is a marked exaltation of the viscosity. There is no doubt that chemical constitution will have a marked influence on the viscosity, as in the case of lubricating oils, where unsaturated linkages raise the viscosity and conjugation of unsaturated groupings is accompanied by decided increase in viscosity.

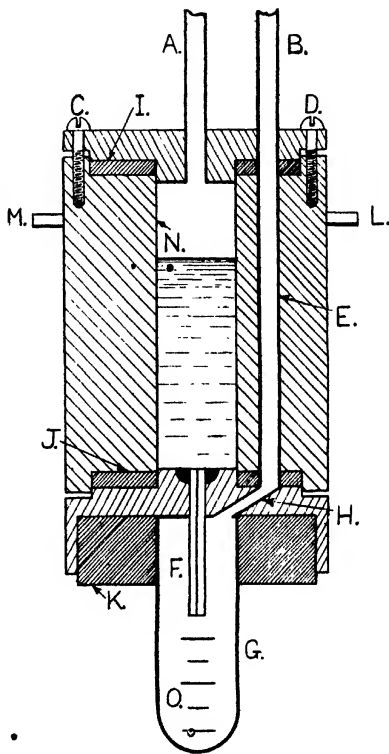


FIG. 35.—Bingham and Greig's Plastometer.

Plastometer.—The viscosity or rigidity may be determined by observing the volume of flow of a fluid through a capillary of known size in a definite time under a known pressure. The rate of flow depends on the pressure and on the diameter of the capillary. Where there is no turbulent flow, a graph for pressure and volume of flow per second will be a straight line passing through the origin. In the case of a plastic body there is a resistance to be overcome before flow ensues; this is expressed as the yield value and is not

observed in the case of true fluids. There are a number of instruments based on the above method, of which Bingham and Green's⁸ is most satisfactory (Fig. 35), although Bawtree's⁹ apparatus (Fig. 36) is simple to use and gives satisfactory comparative results for factory purposes. A defect in Bawtree's apparatus is the difficulty in maintaining an even temperature throughout the liquid. With ordinary oil varnishes the volume per unit time and pressure relationship is expressed by a graph passing through the origin.

The principal parts of the Bingham plastometer are: a container, for holding the material to be tested, into the lower end of which is fastened a capillary; the air pressure system, which includes a stabiliser for maintaining constant pressure; and a flow-meter to measure the rate of flow of the substance as it is forced through the capillary. There is also a water bath for keeping the container at constant temperature and a large air reservoir attached to the system.

The container is made of brass and should have a capacity of 20-30 c.c. It is composed of three sections. The top possesses an inlet and outlet tube. The inlet tube (A) is connected with the air pressure and the outlet tube (B) to the flow-meter. The middle part contains the material to be tested. The bottom part holds the capillary tube (F) and a graduated glass receptacle (G). Enough of the material to be tested is put in the container. The distance from the top level of the capillary to the surface of the liquid is 4 cm. The hydrostatic head which the substance exerts is found by multiplying its density by the length of the capillary tube plus 4 cm. The relationship between viscosity, pressure,

and volume is shown in the expression: $\text{Viscosity} = \frac{KP}{V}$, where P = pressure in mm., V = volume per second, K = capillary constant of the tube = $\frac{\pi r^4 g}{8l}$, and l = length of tube. The readings are obtainable in absolute values.

The Bawtree viscometer consists of a copper vessel A (150 c.c.), which fits into the air chamber of an Abel flash point apparatus.

The tube E (capacity $\frac{50\pi}{4}$ c.c.) has at its lower end an orifice 3 mm. long and 1 mm. diameter. Into the upper cavity fits a ball G at the end of a rod. The knife edge J is to mark where the fluid fills the tube under the pressure of air introduced at D. 100 c.c. of the fluid are put in A and the time is taken for E to be filled under a known air pressure.

Only very small yield values were observed by Gardner and Holdt¹⁰ if the varnishes are properly made, but where the varnishes were stringy and worked badly, a yield value or indication of plasticity was observed. In the case of paints there is always a yield value which varies with the paint. The yield value determines to a large extent the tendency of the material to adhere without running to the surface to which it is applied. In varnishes a yield

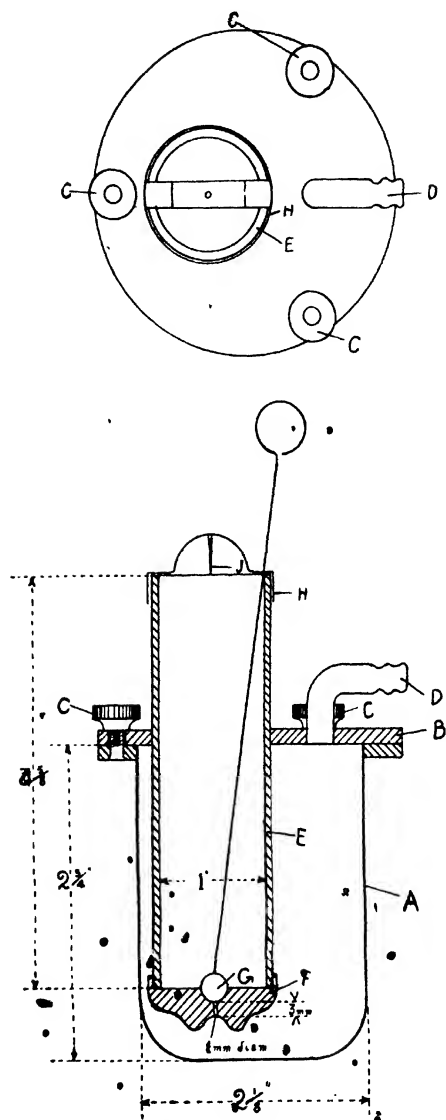


FIG. 36.—Bawtree's Plastometer.

value is unnecessary, as the tendency to run is checked by rapid evaporation and quick setting. If a varnish show any yield value it must indicate a change of the components to give a network of coagulated material, which may have an effect similar to solid friction materials, such as paints and clay suspensions. Black bituminous enamels resemble paints, in that the thicker varieties show definite yield values, and the connection between mobility and yield value resembles that indicated by Bingham and Green. For comparison of stoving enamels it is necessary that the percentage of volatile thinners be as nearly as possible the same.

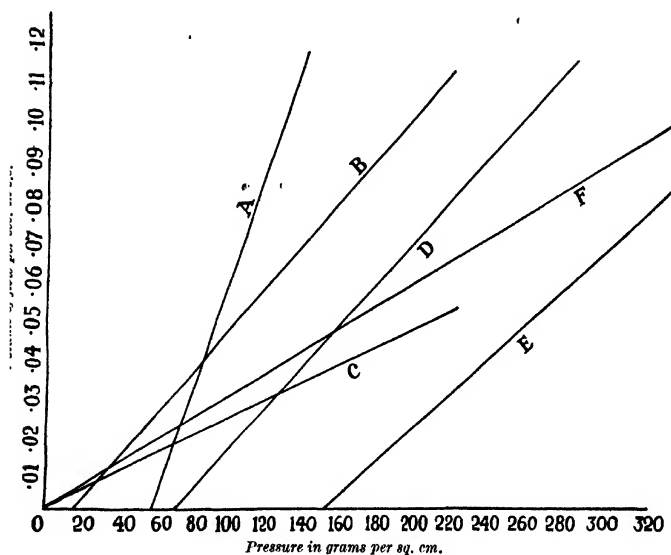


FIG. 37.—Relationship of flow to pressure in Varnishes.

A, B, and C represent the pressure-volume curves of three oil varnishes (Gardner). D and E, black stoving enamels (Bawtree's apparatus). F, Pressure-volume graph of a brushing cycle enamel (Bawtree's plastometer).

Elasticity of Varnishes.—The elasticity of a varnish is a function of the oil content, increasing resin concentration causing brittleness. A method of comparison of the elasticity of long-oil and medium or short-oil varnishes has been investigated by the writer. It consists in applying varnish to one side of a strip of smooth aluminium plate (3" × 1" or 6" × 2" of 28 S.W.G.) in such quantity as to give a dry film between 0.4 and 1 oz. per square yard. The varnish must be brushed on to give an even coat. The plates are hung in a well-ventilated drying chamber and kept at room temperature for forty-eight hours, the varnish drainings having been previously removed from the plates during the first hour of drying. After

drying, the plates are exposed to a temperature of 100° C. for two hours and, after cooling half an hour to allow them to attain room temperature, they are bent through 180° over a quarter-inch rod. A durable elastic varnish for outside wear ought to exhibit no cracks on the bend. This test distinguishes durable outside varnishes from inside varnishes fairly sharply. The ratio of resin to oil must not rise above 0.5, otherwise the film will show cracks on bending.

	Weight of film, oz. per sq. yd.	
Flatting	0.549	Cracks.
	0.293	Slight cracks.
	1.0	Cracks.
Cabinet	0.96	"
Inside oak	0.7	"
Elastic outside	0.9	No cracks.
	0.9	"
Elastic waterproof	0.6	"

H. Wolff¹¹ applies varnish on metal or paper attached to a hinged plate which can be moved through any angle. The apparatus consists of two strips of wood, each having a right-angled edge fastened together by hinges. Strips of tinned iron, parchment, etc., coated with the material to be tested are laid across the wooden strips and fastened down by drawing pins, the strips being slotted to permit relative movement with the wood plates when they are rotated about their hinges. Since an angle 90° represents the smallest angle to which a varnished strip can be bent on such an apparatus, its use is restricted to comparatively "short-oil" varnishes. For the examination of elastic varnishes a modified form of apparatus is used, in which the edges of the wood strips adjacent to the hinges are at an acute angle and an obtuse angle respectively, in order that such edges may meet when the two strips are laid in the same plane. Approximations to the angle of the strip about the edges of the board are obtained from readings on a protractor fastened to one of the strips and by simple formulæ, the acute angle in the bevel in the second apparatus described being previously determined. For testing varnishes, strips are bent on their support and readings taken at various points, *e.g.* local cracking, surface cracking, flaking. In the case of very elastic varnishes, which allow bending to the fullest range of the apparatus without any failure, repeated bendings, after allowing a suitable interval for recovery, furnish numerical data for the comparison of different products. Strips of a varnish of unknown composition were prepared by brushing on one, three, and six coats respectively, the thinning of the varnish in the last two cases was adjusted to give a thickness of coating approximately equal to the first, and strips of the same varnish applied by dipping and spraying were compared. The results showed that the highest elasticity was afforded by the six-coat strip and a sprayed-on coat, which were almost equal. The minimum proportion of castor oil to confer the maximum elasticity on a spirit varnish was found to be 3.4 per cent. It is also stated

that the elasticity of spirit varnishes on addition of castor oil shows the greatest increase with between 0 and 1 per cent of oil.

The Hardness of Varnishes.—The craftsman's method of testing the hardness of varnishes is that of a finger or nail test and is individually comparative. Forms of apparatus have been suggested by Laurie and Bailey, and by Jahns, and are described in most text-books. Laurie's method is dependent on the thickness of the film and is only suitable for short-oil varnishes. The Clemens method is simple, consisting of a small balance with one arm longer than the other, like a Westphal. The long arm carries a point on the under side and a pan on the top. Weights are put on the

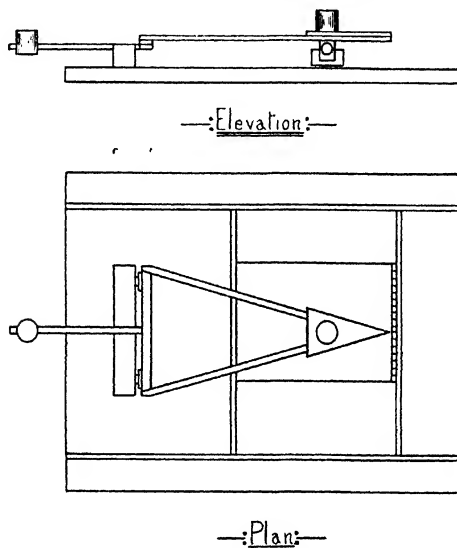


FIG. 38.—Wolff's hardness tester.

pan and the dried varnish coat on glass is put under the point in a holder and then drawn along. The weight required and the nature of the scratch produced are then considered criteria of the hardness. Britton¹² has suggested a list of sixteen crystalline substances of different hardness on the lines of Mohr's scale. When the scratch produced by a crystal is ill-defined or can be removed by rubbing, the film is harder than the crystal used. It must be assumed that the crystals possess uniform hardness. H. Wolff¹³ has devised an apparatus (Fig. 38) for testing the hardness of a varnish, which consists of a triangle, formed by three wooden strips, the base of which is hinged to a base-board. At the apex of the triangle is fitted a blunt knife-edge directed towards the face

drying, the plates are exposed to a temperature of 100° C. for two hours and, after cooling half an hour to allow them to attain room temperature, they are bent through 180° over a quarter-inch rod. A durable elastic varnish for outside wear ought to exhibit no cracks on the bend. This test distinguishes durable outside varnishes from inside varnishes fairly sharply. The ratio of resin to oil must not rise above 0.5, otherwise the film will show cracks on bending.

	Weight of film, oz. per sq. yd.	
Flatting	0.549	Cracks.
"	0.293	Slight cracks.
"	1.0	Cracks.
Cabinet	0.96	"
Inside oak	0.7	"
Elastic outside	0.9	No cracks.
"	0.9	"
Elastic waterproof	0.6	"

H. Wolff¹¹ applies varnish on metal or paper attached to a hinged plate which can be moved through any angle. The apparatus consists of two strips of wood, each having a right-angled edge fastened together by hinges. Strips of tinned iron, parchment, etc., coated with the material to be tested are laid across the wooden strips and fastened down by drawing pins, the strips being slotted to permit relative movement with the wood plates when they are rotated about their hinges. Since an angle 90° represents the smallest angle to which a varnished strip can be bent on such an apparatus, its use is restricted to comparatively "short-oil" varnishes. For the examination of elastic varnishes a modified form of apparatus is used, in which the edges of the wood strips adjacent to the hinges are at an acute angle and an obtuse angle respectively, in order that such edges may meet when the two strips are laid in the same plane. Approximations to the angle of the strip about the edges of the board are obtained from readings on a protractor fastened to one of the strips and by simple formulæ, the acute angle in the bevel in the second apparatus described being previously determined. For testing varnishes, strips are bent on their support and readings taken at various points, *e.g.* local cracking, surface cracking, flaking. In the case of very elastic varnishes, which allow bending to the fullest range of the apparatus without any failure, repeated bendings, after allowing a suitable interval for recovery, furnish numerical data for the comparison of different products. Strips of a varnish of unknown composition were prepared by brushing on one, three, and six coats respectively, the thinning of the varnish in the last two cases was adjusted to give a thickness of coating approximately equal to the first, and strips of the same varnish applied by dipping and spraying were compared. The results showed that the highest elasticity was afforded by the six-coat strip and a sprayed-on coat, which were almost equal. The minimum proportion of castor oil to confer the maximum elasticity on a spirit varnish was found to be 3.4 per cent. It is also stated

of the passage of the metallic ions through varnish films could be detected, although they were carefully tested by means of reagents inserted between the film and the glass or aluminium surfaces. A superficial bloom was observed when varnishes were immersed in solutions of salts, but it could be easily removed, leaving a clear film underneath, and indicates surface corrosion of the varnish. The milky appearance of an elastic varnish immersed in water is due to an emulsion of water in the film, which can be increased or diminished by the presence of special components of a varnish. This emulsion disappears when the elastic film dries, owing to the evaporation of the water. The film regains almost its original

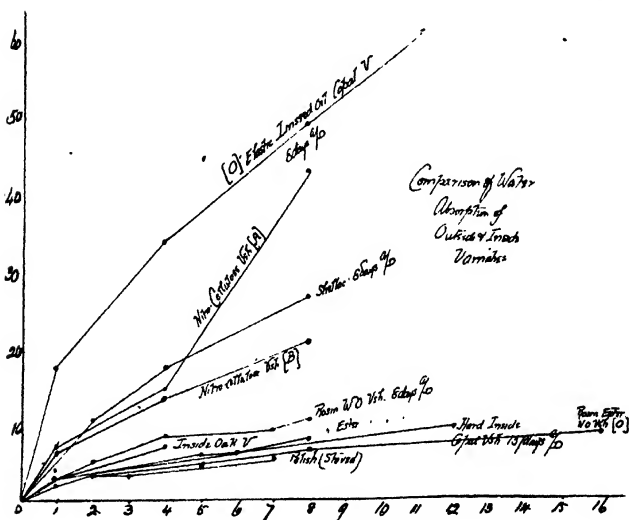


FIG. 39.—Water absorption of varnishes.

weight, but it must be pointed out that on re-immersion in water the velocity of absorption has increased; e.g. a film which has been dried after five days' immersion in water shows on re-immersion in one day an absorption equal to that of the first five days' period of immersion. It would appear as if the capillary passages in the semi-permeable membrane had been permanently enlarged. Alternate exposure to air and immersion in water reduces the amount of absorption owing to the process of oxidation and polymerisation of the components of the film during the periods of exposure. No water-line effects were observed. The varnish films can be weighed rapidly with their charges of absorbed water with an accuracy of not less than 1.5 per cent of the weight of the water taken up. In the case of short-oil varnishes or shellac varnishes

Area of slides—3" × 1"		Average wt. of films—0.14—0.15 gms.						
Time of air-drying. (Days.)		% gain in weight on immersion for—						
		1 day	2 days	3 days	4 days	5 days	6 days	7 days
Distilled water	57	11.1 (white)	16.8 (white)	22.5 (white)	29.8 (white)		51.2 (white)	
N. NaCl	"	3.27 (clear)	2.15 (clear)	3.1 (clear)	3.1 (clear)		1.4 (clear)	1.8 (clear)
$\frac{1}{2}$ N. NaCl	"	4.2 (clear)	5.0 (clear)	4.6 (clear)	5.0 (clear)		4.9 (clear)	5.7 (clear)
$\frac{1}{10}$ N. NaCl	"	9.1 (sl. white)	13.2 (white)	18.6 (white)	23.0 (white)		43.7 (white, blisters)	
$\frac{1}{100}$ N. NaCl	"	11.3 (sl. white)	18.0 (white)	24.0 (white)	31.0 (white)		61.0 (white, blisters)	
N. CaCl ₂	"	1.6 (hvy. bloom)	2.1 (hvy. bloom)	2.3 (hvy. bloom)	1.6 (hvy. bloom)		1.09 (hvy. bloom)	0.5 (hvy. bloom)
N. Na ₂ SO ₄	"	3.3 (clear)	4.7 (clear)	6.5 (clear)	11.0 (sl. white)	13.9 (sl. white)	11.6 (sl. white)	
$\frac{1}{2}$ N. Na ₂ SO ₄	"	5.5 (clear)	7.5 (clear)	10.3 (white)	16.0 (white)	18.8 (white)		
$\frac{1}{2}$ K ₂ SO ₄	8	4.9 (v. sl. white)			4.9 (sl. white)	4.9 (sl. white)		
$\frac{1}{2}$ KCNS	8	3.0 (clear)			1.7 (clear)	2.1 (clear)		

FIG. 40.—Relationship of water absorption to salt concentration.

Average wt. of films—0.14 to 0.15 gm.

Varnish	Time of air-drying. (Days)	% increase in weight after immersion in water for—						
		1 Day	2 Days	3 Days	5 Days	6 Days	12 Days	
Elastic Varnish	137	12.1 (white)	..	16.1 (white)	23.5 (white)	
Elastic Varnish (Turps)	137	12.9 (white)	27.7 (white)	
Hard Varnish	137	4.5 (bloom)	10.4 (sl. cloudy, brittle)	
Elastic, water- resisting Varnish	3	0.3 (clear)	0.4 (clear)	..	1.9 (clear)	..	9 days, 2.8 (clear, elastic)	
Elastic Varnish	8	16.0 (white)	34.6 (white)	..	11 days, 62 (blisters)	
{ 18 hrs. Stoved 4 hrs. at 120°F.		8.5	12.8	16.5	...	29.6		
		(white)	(white)	(white)		(white)		

FIG. 41.—Influence of age of oil varnish films on water absorption.

the turbidity of the film on immersion is permanent, due to the separation of the resin-oil components or to the presence of a resin emulsion in water.

Further conclusions drawn from the investigation may be summarised as follows :

(1) The influence of linoxyn and polymerisation oxidation products in the film on the water absorption is shown by lengthening the period of hardening previous to immersion, or by stoving the varnish or exposing it to bright sunlight or to the light from a mercury lamp. The water absorption power of the unsaturated glycerides is high, compared with the oxidised or polymerised modifications.

(2) The presence of polymerised oil inhibits water absorption.

(3) Excess of metallic driers and bases tends to increase water absorption, as well as the cloudiness of the film, especially if the metals are present in the form of metallic oil soaps and not in combination with the resin.

(4) Resin concentration tends to inhibit water absorption, but after a time the resistance of the film breaks down owing to the separation of the resin components.

(5) Shellac and cellulose varnishes are inferior in water-resisting power to special resin-oil varnishes.

(6) Highly polymerised oil mixings containing neutral resin esters have an exceedingly low water-absorbing power, so that they are almost waterproof. Such varnishes contain China wood oil and rosin esters, and are superior to most paint films in resistance to water.

(7) Lead and manganese seem to act differently in their effect on water absorption. It was thought that lead exercised a polymerising effect on a drying oil, but this cannot be confirmed by experiment, and it must be assumed that it influences either the direction of oxidation of the drying oil or the degree of gelation of the oxidised oil (linoxyn).¹⁵

(8) Varnishes with a low-water absorption show a tendency to "bloom," especially if the superficial drying of the film be strong.

The writer attaches importance to the determination of the water absorption of varnishes.* Water softens the film and tends to make it dust-collecting, so that condensation on damp days occurs, and if dust has become attached to the surface no removal is possible, especially if the evenness of the surface has been affected by the presence of excess of surface driers. Penetration of water reduces the adhesion and will set up interaction between the components of the film. The low-water absorption of an elastic film

* In the determination of the water absorption of varnish films the following precautions must be taken :

- (1) The plates dipped in the varnish must be withdrawn at the rate of 10 secs. per inch.
- (2) The varnished plates must be stoved until constant weight in a current of air of 15 litres per hour.
- (3) It is advisable to use (N/400)NaCl instead of distilled water for an immersion period of 3 days.

denotes a high concentration of linoloxyn. Non-penetration of water combined with elasticity are the requirements of a durable varnish.

The water absorption of a varnish film may also be investigated by methods suggested by de Waele,¹⁶ who, however, has given few details of the results. The films of varnish were obtained by coating tinned iron sheets, allowing them to dry for several days, and then amalgamating one edge of the sheet with mercury and dilute sulphuric acid. In the course of a few hours amalgamation will have proceeded sufficiently to allow the film to be detached. Another method of obtaining detached films is to apply a film of a long-oil varnish on doped linen and, when the film is dry, to soak the whole in water, whereupon the varnish layer is easily detached. H. A. Gardner¹⁷ has investigated the moisture and water-absorbing powers of varnishes and enamels on different kinds of wood. Three coats of varnish were applied to the bare wood, and after a period of ten days' air-drying the panels ($4'' \times 8'' \times \frac{1}{2}''$) were exposed for seven days in a moist chamber, weighed, subsequently immersed for seven days in water, and, after removing superficial water, the panels were again weighed. The following are a few of the results:

	Moisture, oz. per sq. yd.	Water absorbed, oz. per sq. yd.	Water retained after drying, oz. per sq. yd.
Bare wood (spruce)	7.04	37.83	1.45
Raw linseed oil, wood panel .	6.01	23.2	2.18
Nitrate dope	4.18	21.5	4.7
Pigmented oil dope	2.04	5.45	3.02
Shellac	0.52	1.48	1.21
Spar varnish	0.87	0.5	0.32
Enamel containing spar varnish	0.13	0.68	0.36

Wood contains ordinarily 11-15 per cent of moisture.

Defects of Varnishes.—It is not surprising that with such complex and delicately constituted combinations as copal or bituminous varnishes great liability to defects after manufacture are experienced, unless control under strictly regulated conditions be insisted on. The lack of knowledge of the reactions involved and of the properties of colloid solutions, as well as of their surface characteristics, is such that defects in varnishes are very common. Many of the so-called defects may be traced to (1) improper or low quality materials; (2) careless or inexperienced conditions of manufacture; (3) variation in atmospheric conditions.

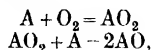
Cracking of the Film, Flaking, etc. (Vernis crevassant; Springen. Reissen oder Brechen der Oberfläche).—Sometimes the previously elastic film of varnish may harden and become so brittle that cracks will appear, more especially if variations in the atmospheric temperature have been severe. The elasticity must be carefully considered, so that during the hardening the flexibility

must be as great as possible to stand exposure to the sun ; whereas in a situation sheltered from extremes of temperature the hardness must be as great as possible to withstand reasonable wear and tear. The presence of too high a gum-resin content for the requirements will favour the formation of cracks. Cracking of a film due to this cause usually manifests itself without any other attendant phenomena. If after a period of exposure the film assumes dullness, which appears as an iridescence when viewed in bright sunlight, the loss of lustre is due to the destructive oxidation of the drying oil, especially when over-treated with driers and not previously polymerised. An examination of the surface will show a network of fine cracks, at first of microscopic size. This is noticeable in linseed oil varnishes far more than in those containing China wood oil or stand-oil. Occasionally wood oil varnish films may show cracks due to the presence of an excessive amount of rosin, without loss of lustre. The rapid and progressive oxidation of the drying oil will result in a loss in weight beyond the point of maximum increase, with a resulting contraction in volume. A rarer cause of cracking arises from the application of the coatings in the wrong order ; e.g. the application of a relatively less elastic undercoating on the top of a finishing varnish, whereby the less elastic superficial layer is unable to withstand extremes of temperature. Cracking may also be due to a lack of adhesion between varnish films ; e.g. a coating of oil varnish on shellac may crack owing to uneven expansion and contraction of the two layers. Cracking may also be due to application upon a layer incompletely dry or too thick. More attention should be paid to the rate of expansion or contraction of the materials to be covered, as well as to the protective undercoats and to the general adhesion to the surface. The flattening or keying of coatings acquires increased importance when viewed from this standpoint. There is no definite information available beyond the results of experience, and further consideration would be valuable, as well as a study of the slow devitrification of gum-resins on exposure either alone or incorporated with oil. It is evident that the above defect is due partly to faulty manufacture and partly to neglect of precautions on application. A paint undercoating, containing pigments which accelerate the drying of oil, if not properly hardened, will cause catalytic oxidation of the finishing coat and hasten cracking due to the diffusion of the drier.

Wrinkling, Rivelling (vernis ridant, striant ; Falten- oder Runzelziehen). -This appears as a puckering of the varnish film where a thicker layer has collected owing to flow. With the exception of short-oil varnishes, which harden more by evaporation of solvent than by oxidation, it is a defect which will appear when the film has been carelessly applied. Expansion in volume of an oil occurs simultaneously with absorption of oxygen followed by a contraction in volume of the film, but the increase in specific gravity does not correspond with the weight of the oxygen absorbed.

Varnishes showing a tendency to skin-over in bulk often wrinkle

on application. The formation of wrinkles is an indication that the second part of the reaction, .



indicating transference of oxygen from the surface layer to the under part of the film, is incomplete. A hypothesis is put forward by H. Wolff,¹⁸ who points out that the rate of oxidation of a thick film of varnish is greater on the surface than in the body of the film, owing to the non-penetration of the activating ultra-violet rays. Expansion with approach to completion of solidification will occur on the surface independently of and in advance of the under layers. The defect is especially noticeable in varnishes containing cobalt and manganese (surface driers), as distinct from those containing lead and cerium,¹⁹ especially if the cobalt and manganese are present in excess. The thinners also play some part in the phenomenon of wrinkling. H. Vollmann²⁰ found that varnishes prepared on the same base, using as thinners turpentine, solvent naphtha, tetraline, petroleum (b.p. 128°-176° C.), primary benzol (b.p. 66° C.), and petroleum (b.p. 65°-94° C.), remained, with two exceptions, practically free from wrinkles when kept under red glass or in the dark for six months without free access of air. The two exceptions (benzol and low boiling point petroleum) were more wrinkled under white light than in the red light or in the dark, but remained perfectly smooth in the chamber where there was no free access of air. The use of highly volatile thinners is conducive to wrinkle formation. The lack of free access of air might have prevented wrinkling through slower evaporation of the solvent and slower oxidation of the drying oils. Immature varnishes may show rivelling.

Pinholing or Pitting (Nadellöcher).—The surface shows numerous depressions due partly to deposition of particles from an insufficiently matured varnish. The nuclei are generally gum-oil particles which are floating in the varnish due to defects in manufacture or to the use of excess of non-solvent thinners. Warming or addition of a true solvent will generally remove the effects, or the particles will be slowly deposited on tanking. Improper mixing of varnishes will often produce pitted surfaces due to the separation of some components of the mixing. Oils free from foots and break, asphaltum and bitumens, which are freely soluble after cooling, carbon blacks, finely ground and free from grease and mineral spirits of proper rates of evaporation, must be selected to avoid pitting and crater formations in black Japan films.²¹ The cause of pitting in black Japans is considered to be stearine from varieties of stearine pitch, and may be avoided by use of lighter grade petroleum.²²

Cissing (vernis repoussant un gras; kriechen).—This term is used to describe the phenomenon occurring when oil is applied to a damp surface, or *vice versa*, and consists in the contraction or retrogression of the film to produce separate drops of lesser surface. It indicates the existence of high interfacial tension

between the varnish film and the surface, which may be another varnish or a metal or a pigmented surface. Cissing usually occurs after the application of a varnish film to a glossy undercoat which has not been properly rubbed down by pumice powder to provide a "key" to the following coat. Sometimes a film will dry to an even surface in the air, but on stoving the defect appears, especially if the mixing contain gum-oil particles in suspension. The defect would appear to be connected with the rate of evaporation of the volatile thinner, as well as with its solvent properties, because, if the volatility of a petroleum thinner be reduced by addition of turpentine, cissing may be prevented.

The inhibiting effect of flattening is probably accounted for by the modification of the "angle of contact" consequent upon the roughness of the flattened surface. Cissing may also be prevented by varnishing over the undercoat, which is still on the tack, *i.e.* before it is quite hard and dry; and then more complete contact takes place owing to a slight mutual solubility of the upper and under surfaces. It may even occur when rubbing down of the undercoat has been done, and is attributable to the newness of the varnish, which need not be so new as to be cloudy. It is probable that the microscopic dispersed particles which separate on the rapid evaporation of volatile solvents act as nuclei similarly charged to the bulk of the medium, and consequent repulsion around the nuclei takes place or selective absorption of the components of the film. The remedy is the addition of a solvent which will hold the microscopic particles dissolved until the film has set. The explanation of cissing is occasionally difficult, but the sweating through of an immiscible component of a previous undercoat, *e.g.* a bituminous undercoat, may be the cause. Washing of the undercoat with dilute sodium carbonate or rubbing it over with whiting may remove any danger of cissing.

Bubbling.—The appearance of small bubbles during application of a varnish, changing subsequently to pinholes, is a trouble generally due to too rapid an application. Too low a viscosity owing to excessive thinners favours the formation of bubbles, which consist of air entrapped within a rapidly drying thin varnish film.

Blistering and Peeling (verniss sautant, s'écaille; Blasenziehen).—These are due to the same cause, *viz.* enclosure of ultimately volatile or even gaseous products within varnish films. A soft undercoat of paint containing oil or fat of a non-drying character is considered to produce by its expansion a swelling of the surface. Water may also be the cause, it being absorbed during the flattening down and not expelled before the application of the next coat. Reference to the water-absorbing properties of varnishes will show that this explanation is most probably incorrect, owing to the comparative permeability of the varnish film to water. Solid impurities, often metallic soaps (driers), arising from imperfect maturing of the varnish, set up local points of decomposition of the oxidised film immediately in contact with the undercoat, with development of gaseous products of decomposition, which are unable to penetrate

the surface film. These gaseous products may arise from the action in the undercoat of driers which often contain water. Exposure to the sun or stoving in a damp atmosphere on a soft undercoat encourages the formation of blisters for the reason just given. Generally the commonest cause of blistering is to be found in the inadequate hardening off of the undercoat before the application of the finishing varnish. The examination of transverse sections of blisters of paint films would be of value.

Peeling is the result of the application of a varnish coating on an undercoat containing too much drier, for the reasons given above as to the cause of blisters formed round the nuclei of particles of drier. This defect will not occur if the surface has been properly rubbed down previous to the application of the finishing coat.

*Chalking (verniss blanchissant).**—The whitish translucence of a varnish film on immersion in water is due to an emulsion of water in the film, provided that the opacity disappears on removal from the water and subsequent air-drying of the coating.²³ It is most marked in elastic linseed oil varnishes, and its intensity is a function of a number of variables which have been referred to under the water absorption of varnishes, viz. the thin-oil content, the amount of basic oxide, lead or lime, and the age of the film, i.e. the amount of linoxyn or polymerised components in the varnish. The presence of polymerised oil or China wood oil inhibits the opacity, and the neutrality of the mixing has the same effect. Some authorities state that chalkiness is not detrimental to the durability of the film, but it must be admitted that the formation of an emulsion will affect the adhesion of the film to the surface. If varnishes of an elastic character can be produced which remain clear in water, they ought to be preferred. The danger of the surface becoming spotted, due to the imprisonment of the emulsified water noticeable in fresh varnish films, is serious. The older a film is before it is exposed to moisture, the smaller will be the amount of water absorbed and the less the intensity of the whiteness. It is generally advisable for a varnish to have as long a period of air-drying as possible before it is subjected to the action of water. To avoid the defect of chalking, certain important principles must be adhered to in dealing with elastic varnishes :

(1) The water absorption must be low, i.e. the proportion of polymerised oil must be as high as possible, a fact which favours the use of China wood oil, and the polymerised oil must be capable of drying hard and free from tack.

(2) If thin linseed oil be present, the amount of lead, lime, or other metallic oxides must be reduced as much as possible, or the metals must be in combination with the gum acids in the film.

(3) If the acidity of the resin be reduced the reduction must be brought about by transformation into a non-emulsifying ester. The presence of lime in rosin produces chalking.

The use of rosin or rosin esters in China wood oil varnishes has produced films which show no opacity in distilled water.

* Chalking of varnishes must not be confused with "chalking" of paints.

H. Wolff²⁴ has experimented with varnish surfaces exposed to the action of water, the water being varied with respect to dissolved air and oxygen. He concludes that any action which attended the experiment was due solely to the water and not to the dissolved gases.

In sea water chalking is much less pronounced, and it is quite easy to remove the milkiness from a film by soaking it in N.NaCl solution, which will reduce the water absorption to a low value.

The presence of substances which increase the water absorption will tend to increase the milkiness. The addition of a lead drying oil, although diminishing the wetting power of the surface, is found to increase the water absorption and the opacity of a film. It must be noted that lead in a polymerised oil varnish or added in the form of a resinate does not produce a marked chalking effect, partly owing to the nature of the oil and partly to the slight water absorptive power of the film; moreover, it is possible to introduce into a varnish substances which inhibit the emulsification of the absorbed water. The addition of wax (Carnauba or beeswax), which does not remain in solution and gives a cloudy film, is found to have no effect on the water absorption, although the surface tension of the film to air is greatly increased. With increased gum content the milkiness is reduced, provided that emulsifying metals are absent, so that in the case of a "polish" the water absorption is much reduced, and the film remains clear on immersion in water for a very much longer time than in the case of an elastic varnish.

In the case of shellac or spirit varnishes containing resin the water absorption is comparatively high and chalking appears quickly, and does not disappear when the film is removed from the water and allowed to dry in the air. The opacity is permanent and the emulsion formed is one of the resin as the disperse phase, in contradistinction to the emulsions of the elastic oil varnishes which contain water in the disperse phase.

Bloom (Vernis volant; Wolkig- oder Nebligwerden).—Much has been written on "bloom," and no agreement as to its cause has been reached. The problem is, however, closely related to that of chalking, and affords an interesting example of the application of the principles of the physics of the surface. The explanation put forward by the writer considers, firstly, the changes occurring during the drying of a varnish film, and secondly, the changes which occur after it has set hard.

Drying is an oxidation and gelation process, and the products depend on the nature of the driers employed, as lead acts in one way, manganese and cobalt in another. Extensive oxidation of the drying oil by superficial driers (manganese and cobalt) will tend to produce a superficial film of linolein, which will subsequently become uneven. The part played by the drier is an important factor in the consideration of bloom. The first stage of blooming is the production of a veil or superficial bloom due to a film of moisture and dust which has collected on the microscopically

uneven film, and which retards the thorough oxidation of the film, while the dust becomes embedded in the moisture-softened surface. If this bloom be washed off soon after its formation, a clear surface is left, but it may be covered again by more bloom, also removable by water, leaving a bright surface, which may or may not become dull, depending on the nature of the varnish. If the veil be not removed by washing, the film of water continues to gather dust and will gradually penetrate the varnish coating and cause a change in the dispersion of the resin-oil component of the linoxyn with loss of transparency. The amount of water absorbed is so small in quantity as to be unweighable. This permanent bloom does not disappear under the ordinary variations of temperature. By addition of suitable inhibitors of dispersion changes to the varnish during its manufacture, and by the incorporation of substances which preserve the smoothness of the surface and prevent condensation of moisture, it is possible to prevent temporary and permanent blooming in either linseed oil or China wood oil varnishes. It must be remembered that the presence of any ingredient which will interfere with the uniform setting of or produce a change in the film surface subsequent to setting will favour condensation, so that the introduction of viscous oil into a varnish mixing may produce bloom. The causes of blooming as set out by the writers of varnish text-books are many and varied.

Coffignier states that varnishes become white owing to the presence of resins of inferior quality, *e.g.* rosin, or to excess of driers (*verniss blanchissant*). Bloom (*verniss voilant*) may be due to insufficient sweating of the resin, lack of elasticity of the varnish, foul gases in the air, or too rapid exposure to moisture before hardening. "Si le beau brillant est obtenu avec une résine de qualité inférieure il ne tarde pas à disparaître, la surface devient mate et quelquefois les vernis *blanchissent*, et ne restent pas sur l'objet qu'ils recouvrent. Sous la simple action de l'humidité ou de la pluie le même phénomène peut se produire. Dans ce cas, on peut être certain que le vernis est à base de colophane" (this apparently applies to chalking). "Quelquefois le brillant disparaît par suite de la production d'une sorte de buée à la surface qui paraît recouverte d'un brouillard; on dit que le vernis *voile*. Or, on a constaté le fait avec de bons vernis. Il peut se produire s'il y a condensation de l'eau pendant le séchage ou sous l'influence de certains gaz contenus dans l'air. Une mauvaise cuisson de gommes laissant des corps huileux peut conduire à des vernis voilants; mais s'il est possible de trouver des explications pour certains cas, il en est d'autres où, au contraire, il est à peu près impossible de savoir pourquoi un vernis a voilé."

According to the explanation given above it might be considered that the acidity of the film is a factor in the condensation, and by acidity is meant the water-soluble acidity arising from the resin or the oxidation products of the oil. Manganese and cobalt will be more active in producing bloom than lead driers, and similarly a short-oil varnish containing manganese and cobalt will condense

water more readily than a long-oil varnish containing lead. Certain long-oil varnishes are, however, able to condense water and to bloom. The changes in the water-soluble acidity of a film of dried varnish not containing lead has been referred to elsewhere, and it has been found that the values are far higher than those of the original varnishes. The water-soluble acids are volatile, as is indicated by the reduction in their amount after the film has been exposed to mercury vapour light, and also in the reduced condensation on exposure to moisture after the mercury light treatment. Nevertheless, it has been found that the water-soluble acidity is not a factor in either condensation or bloom.*

Wolkig-, Rauchig- oder Nebeligerwerden (reifig), Anlaufen, Hauch bekommen, are the terms used in Germany to describe the same phenomenon.

Seligmann and Zieck (p. 793) state: "Die wahrscheinlichste Ursache ist die Kondensierung von Feuchtigkeit auf der noch nicht erhärteten Lackschicht."

In damp climates bloom is more frequent than in dry, and can in many cases be removed by washing. From the writer's experience, bloom can be detected in a few days at any time of the year by the mist formed on a dry film of the varnish on glass partially immersed in water. It can occur with the same varnish in one place and not in another. The colours in varnish exert no influence on the bloom. Weathering is said to be a factor, and the content of low quality resin is said to make the film hygroscopic. The preparation of a non-blooming varnish requires experience and knowledge of varnish components.²⁵ The control of uniform and regular setting and hardening of the film depends on a number of factors: moreover, separation of material in the film itself may affect the evenness of the surface and produce condensation. It would appear also that the presence of substances which by their action will produce the slightest degree of unevenness of the film will produce surface condensation, and in most cases bloom is traceable to such a cause. Microscopic silkiness must occur before condensation appears.

An American explanation of blooming or blurring is that due to poor material, but in wet weather the trouble may appear on the best possible finish, although it is usually corrected by washing the film with water and allowing it to stand in the sun. In the opinion of the writer the influence of turpentine substitutes in encouraging bloom is very doubtful. The old practice of washing down a varnish film with water a few days after application removes the film of dust and moisture held by the superficial acids which retards the hardening of the surface.

It is advisable to ventilate rooms in which varnish work is being done, and to keep the floors dry and free from dust.

* Chalking and bloom are closely connected in the short-oil resin varnishes and appear to indicate a change in the dispersion of the resin oil component. The temporary chalking of long-oil varnish films is due to emulsion of water in the film, which disappears when the film dries.

Webbing, or Crocodile Skin.—This defect appears at first sight to simulate cracks, but it is really due to a puckering or rivelling of the surface, the excess of film being drawn up into ridges which form the boundaries of a pattern work. It occurs when China wood oil is present in a varnish, especially when the oil has been insufficiently cooked or polymerised during its incorporation; moreover, it depends on the conditions of drying; e.g. in the dark or in the absence or low concentration of ultra-violet rays. The webbing may appear in an atmosphere highly charged with carbon dioxide, although under ordinary conditions it may not occur. Since so many varnishes now contain wood oil, a webbing test is of considerable importance. The test adopted in the British Standard Specifications for Aircraft Materials (2 X 6, 1920) is as follows: The apparatus consists of a copper oven, $15 \times 15 \times 15$ cms., having a hole 3 cms. diameter in the middle of its floor and containing a perforated copper shelf placed centrally. At the top of the oven are two tubulures, one of which is left open, while the other is furnished with a cork through which passes a thermometer with its bulb reaching to the central shelf. A micro-burner, 4 mms. internal diameter, giving a luminous flame 12 mms. high, is placed underneath the hole in the oven floor, at such a distance that the tip of the flame is about 8 cms. from the plane of the floor. By this means, with an outside temperature of about 14°C . (57°F .), a temperature of about 38°C . (102°F .) will be maintained at the shelf of the oven. Glass plates (e.g. microscope slides) coated with the varnish to be tested, drained vertically for half an hour and the bead removed, are then placed upon strips of cardboard of the same size and dried on the central shelf of the oven, care being taken not to cover up the perforations in the shelf.

Similar irregularities of drying have been noticed in the case of perilla oil. The defect is caused by differences in surface energy of the components and their rates of superficial oxidation. The presence of a more rapidly oxidisable component in a drying oil may often cause the film to assume a pattern-like arrangement, which may be circular in the case of an oil or irregular if a resin is present.

Curdling or Ropiness.—These terms are used to describe changes in viscosity on storage or chilling. They are noticeable on application of a varnish by the production of an uneven surface. Generally they must be connected with changes in the colloid dispersion accompanied by changes in viscosity. The defect may go farther, when it is described as "livering," where there is a general separation of a gum resin-oil component. By addition of raw or boiled linseed oil, spirit or other varnishes, marked viscosity changes may occur, culminated by an actual separation of a gum-oil-thinner complex from the system.

There are a number of terms in use descriptive of varnish defects, of which a few additional may be mentioned:

* *Silkiness (vernis striant; seidenartig).*—This is allied in some respects to ropiness, and appears as a general fine striation of the

surface caused by excess of drier or by lack of flow due to chilling (cf. bloom).

Sweating up of a varnish film (*vernis suintant*; *Schwitzen*) is caused by the too early flattening of a varnish coat before it has had time to harden; or a soft varnish containing too much oil will, after being flattened, lose its roughened dull surface and become lustrous.

Sinking-in of the film, sleepiness (*vernis s'enfonçant*; *Einsinken, Schläfrigwerden*), may be caused either by excess of volatile thinner or by the application of a varnish on a layer which is incompletely dry.

Mottled Surface.—This is very marked when a short-oil or hard varnish is sprayed on an iron plate. If the varnish be warmed slightly before introduction into the spraying pistol the defect will generally not occur, because the globules of varnish will possess sufficient fluidity to coalesce.

Turbidity.—The clouding of varnishes either during the course of manufacture or after the varnish has been kept for some time is a well-known defect. A turbid varnish is looked upon with suspicion as indicating an excess of drier, but nevertheless a clear varnish may become turbid on standing, even if a drier of the best grade and in proper quantity has been employed. Lead resinates, like lead linoleate, will give cloudiness, because it reacts with the free fatty acids in the linseed oil or other oils employed, and the precipitate in the presence of linseed oil always contains lead stearate. Deposits are, however, not formed if proper precautions are taken when lead resinate is used as a drier. The presence of mucilage in the oil may act as a protective colloid and retard the separation;²⁶ moreover, it has the power of absorbing or retaining water, influence of which on chemical changes must not be neglected. It must be pointed out that the acidity of the oil in the varnish mixing must be considered if lead resinate be used as a drier. Generally the acidity due solely to the resin tends to preserve the brilliancy of the varnish mixings, whereas neutrality of gum-oil mixings is unfavourable in that respect, especially when metallic driers are present in any quantity.*

Durability of Varnishes.—From what has been stated in previous chapters it is evident that the drying oil confers durability on the oil varnish film, the function of the resin being essentially to give gloss and hardness. The presence of polymerised oil improves the wearing properties, and the combination of polymerised and oxidised oils in a film is most favourable for durability. The degree of coagulation of the linocyn or polymerisation, for want of a better name, would seem to be conditioned by the nature of the metallic driers, and there is much evidence in favour of the coagulation of the oil deciding the resistance of the film to weathering agencies. Long-oil varnishes are generally more durable than short-oil, the latter containing a higher percentage of resin, which is relatively

* Turbidity may be caused by reduction of the dispersion of the resin in the oil varnish mixing, and it may often be removed by suitably increasing the acidity of the system.

inelastic and often prone to disintegration, due to oxidation or to a transformation from the vitreous to the crystalline state. Chalking in water does not necessarily indicate a bad varnish, but there is a softening of the film due to absorption of water and a strain caused by the swelling from which the film does not completely recover when it dries; moreover, the adhesiveness of the film is weakened. The minimum water absorption and the maximum elasticity of a varnish film have been put forward by the writer as tests for durability, although they cannot completely replace the lengthy period of exposure to the air, which is the only real and satisfactory test. The minimum water absorption in an elastic varnish indicates the proportion of linoxyn on which the durability of the film depends. Water absorption and elasticity do not take into account the oxidising influence of weathering, although the presence of air in water has been shown to have no more effect than the water alone. Possibly the effect of immersion in dilute hydrogen peroxide is worthy of study. A good long-oil varnish film ought not to perish on exposure for a year, although its lustre will have depreciated, and in the China wood-oil classes films ought to stand for eighteen months or two years without appreciable loss of lustre, although a fine cracking of the surface is often noticeable. It may be of interest to refer in greater detail to American tests for durability which have been mentioned in connection with the British Aircraft Specifications for outside varnishes. In the specification U.S. Naval Spar Varnish (No. 3, March 1, 1918) the following details are given of a durability test:

The varnish shall be applied, in three coats, to two unfilled panels of maple wood. The panels must not be less than $5\frac{1}{2}$ in. wide by 18 in. long by $\frac{3}{4}$ in. thick. The first coat of varnish, after drying indoors for three days, shall be lightly sandpapered with No. 00 sandpaper before the application of the second coat. The second and third coats of varnish shall be allowed to dry three days indoors, but neither coat shall be sandpapered or rubbed. A protective coat of varnish (not for test purposes) shall be applied to the back and edges of the panels. The duplicate panels shall then be placed out-of-doors at an angle of 45 degrees to the vertical and facing south.

The durability of the varnish on the test panel must be equivalent to that of an approved varnish under the same conditions.

The importance of the nature of the undercoats in influencing the durability of varnishes must not be forgotten, especially if iron plates be used in the trials.

It is evident that considerable time of exposure would be necessary to produce deterioration in the case of high-class varnishes, and the test is accelerated if the varnish film be applied on a painted thin iron plate. In the U.S. Army Specification for spar varnish an interesting test, viz. the Kauri Solution Test, appears.

Kauri Solution Test.—The Kauri Solution Test is made, by proportionately reducing the elasticity of the varnish under test by a solution of No. 1 "run" kauri in pure spirits of turpentine.

Directions are given for the preparation of the kauri solution, in which the resin is distilled at a temperature of 371°C . until 25 per cent of its weight has been driven off. The residual resin is dissolved in twice its weight of turpentine at 149°C . In carrying out the test the non-volatile content of the varnish under test must be determined. To 100 grams of varnish are added an amount of the kauri solution equivalent to 50 per cent by weight of the non-volatile matter in the varnish. Flow a coat of the varnish thus reduced, on a 4×5 in. panel of 100 lb. tin. Allow the varnish to dry in a nearly vertical position at room temperature for one hour. Place the panel in a horizontal position in an oven and bake for five hours at a temperature of 93° - 100°C . Remove the panel from the oven and allow it to cool at room temperature for one hour. Place the panel over a $\frac{1}{8}$ -in. rod and bend it double quickly. The bending should be done at room temperature (21° - 27°C .). The varnish must show no signs of cracking at the point of bending.

The writer is in general agreement with the importance of this elasticity test, which is restricted to spar or boat varnishes, but the statement by certain American authorities that there is no possibility of a varnish, which is capable of standing the kauri solution test, failing under actual exposure trial cannot be generally accepted.

Water Test.—Another American test in connection with the durability of varnishes is the water test. A bass wood panel is filled with a coat of drop black in oil, thinned with turpentine and drier, and allowed to dry for at least ten days. A coat of varnish is then applied, allowed to dry for forty-eight hours, and lightly sandpapered. A second coat of varnish is then applied and allowed to dry for seventy-two hours. The panel is inclined at an angle of 45 degrees and a gentle stream of cold tap water allowed to flow down the middle of the panel for forty-eight hours. The varnish must show no whitening, dulling, or other defects after any deposits due to tap water are wiped off with a chamois skin.

Similar results may be obtained when one coat of varnish is flowed on a panel of clear window glass thoroughly cleaned with benzol, allowed to dry for forty-eight hours, and immersed in distilled water at room temperature for forty-eight hours. The varnish must not show any whitening or dulling at the instant of removal of the panel from the water.

The conclusions drawn from the above water test are not of real assistance in determining the durability of varnishes. There are many excellent varnishes on the market which will not stand the American water test, and it has been shown in a previous chapter that the chalking of the varnish film may be brought about by the presence of small quantities of metallic substances which are not detrimental to the life of the varnish. If the American spar varnishes are to be restricted to those of the tung oil class, then the water test is more reliable, but it will certainly break down if the above percentage of linseed oil in the mixing be considerable.

The factor of neutrality of a varnish or of its components is

worthy of consideration. Generally a neutral varnish will be more resistant to the action of the weather, but neutrality by addition of metallic oxides will cause brittleness and subsequent disintegration due to hydrolysis of the resin salts and the action of carbonic acid thereon; moreover, the dispersion of the resin is modified, and slow thickening of the varnish mixing will ensue. Neutralisation of the resins by glycerine is desirable in conferring elasticity, although reducing hardness, but the solubility of ester gums in oil is less than that of the resins.

From what has been stated under the defects of varnishes it is evident that a mixture of gum oil and resin is a very sensitive combination. The durability is conditioned by the properties of the resin linoxyn gel which is left after the film has set. The writer has put forward the view that the elasticity of the film and its water-resisting properties are prime factors in foretelling the durability of a varnish film. The examination of the elasticity by the methods already described or by the kauri constant test are generally admitted to be of great value. The water absorption test is indicative of the adhesion of the film to the surface, as well as of the possibility of action of water with the components of the film, chemical or physical, in the production of emulsions of water in oil or separation of the resin in the film. In the case of long-oil varnishes the water absorption indicates the degree of linoxyn formation in the film under the conditions of testing. The presence of driers in great quantities accelerates emulsification, setting up strains in the film and weakening the adhesive power. The influence of the ash content (metallic driers) must be considered.

The following figures will show the connection between the ash-content, elasticity, and durability of a number of varnishes:

	Percentage Ash (Gum and Oil Content).	Elasticity.	Durability.
A	1.96	Good.	Fair.
B	1.39	"	Good.
B	1.48	Fair.	Fair.
C	0.06	Brittle	Poor.
D	1.36	Elastic.	Very fair.
E	2.9	Brittle.	Poor.
F	0.12	Elastic.	Good.
Special	1.8	"	Poor.

The characteristics of a durable varnish are:

- (1) Elasticity of the film; the ratio of resin to oil must not be greater than 1:1.6.
- (2) The water absorption must be low and must not exceed 8 per cent after three days' immersion in N/400 NaCl.
- (3) The ash content must be low. It ought not to exceed 1.5 per cent on the gum and oil content.
- (4) The acidity of the varnish must be low. It ought not to exceed 20.

(5) Consistent with flow, time of drying, and hardness, the amount of thick oil must be as large as possible.

H. Wolff²⁷ has found that neither the action of light nor temperature are nearly so harmful in the weathering of paints as is mist or dew. The condensation of moisture on the pigment or on the underlying material is very harmful.

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CHAPTER XV

SPIRIT VARNISHES

General Characteristics. — Spirit varnishes are distinguished primarily from oil varnishes, in that on the evaporation of the solvent the resinous constituent imparts to the film its own characteristics without the influence of the drying oil requiring oxygen for attainment of a firm linoleum film. Generally, they consist of a resin or a mixture of resins, natural or artificial, or soluble cellulose derivatives, and the process of drying on application to a surface consists essentially in the evaporation of the solvent. Ordinarily the time of drying is much shorter than that of oil varnishes, but a few of the spirit varnishes, *e.g.* spirit soluble Bakelite, require stoving to give hardness or insolubility in solvents. The resins, with their lustre and hardness, are not usually elastic, and very rarely possess the toughness which will fit them for hard wear. Some improvement in the elasticity of spirit varnishes can be obtained by the addition of certain substances which, however, often diminish their hardness and wearing properties. Spirit varnishes are especially suited for the preparation of coloured varnishes, owing to the easy solubility of most aniline colours in methylated spirit. The character of the solvent varies with the dissolved material. Methylated spirit is the commonest solvent, together with less volatile alcohols; *e.g.* butyl and amyl alcohol (fusel oil), and benzyl alcohol ketones (acetone and homologous ketones, acetone oils); esters (amyl acetate, methyl and ethyl acetates), hydrocarbons (benzol, toluene, and xylene) are also used. The solvents proper are often diluted with non-solvents, *e.g.* petroleum or nitrobenzol, in order to produce a mixing of suitable viscosity. It is found that the solid component of a spirit varnish is often soluble in a mixture of two liquids, although it is insoluble in either of them separately. Softening substances are often added; *e.g.* castor oil, which is soluble in alcohol, or triacetin and phenylphosphates, which are incorporated with cellulose acetate in dopes.

The principal solvents for the resins have been already referred to in Chapter VIII.

Preparation. — The description of the preparation of spirit varnishes, which consist of a solution of a resin in alcohol, is very simple. The first method consists in stirring the resin in spirit in

an open vat until it is dissolved and the insoluble impurities, bark, wood, etc., are allowed to settle or are separated by filtration. The solution of the resin can be accelerated by digesting in a wooden barrel fitted with a manhole for charging, the barrel being rotated about its horizontal axis either on geared spindles or on trunnions. Another method consists in dissolving the resin in spirit in a closed steam-jacketed digester fitted with a stirring gear. Although hand-stirring appears primitive, it is claimed that paler varnishes are thus obtained, owing to the reduced contact with air to which the varnish is subjected.

The clarification of the freshly prepared spirit varnish is effected either by sedimentation or filtration; in the latter case special precautions have to be taken owing to the volatility of the solvent, especially if centrifuging be employed.

Craftsmen's details as to the methods of application of spirit varnishes, the preliminary preparation of the wood, and instructions for French polishing, are given in Bitmead's *French Polishing and Enamelling*.¹

Shellac Varnishes.—Shellac is one of the most important constituents of spirit varnishes, as it possesses a degree of hardness and elasticity distinguishing it from all other gums and resins. In a former chapter full reference has been made to the varieties which are employed in shellac varnishes. A number of formulæ are here given in illustration of the uses to which shellac varnishes are put.

Knotting Varnish.—As a damp-resisting coat or to cover knots in wood: Orange shellac 112 lb., medium rosin 56 lb., methylated spirit 28 galls.; or, button lac 84 lb., orange lac 84 lb., methylated spirit 30 galls.

Storing Brass Lacquer.—Button lac 112 lb., sandarach 6 lb., gamboge $\frac{1}{2}$ lb., dragon's blood 3 lb., methylated spirit 30 galls.

Silver Brassfinishers' Lacquer.—Bleached lac 24 lb., sandarach 6 lb., gamboge $2\frac{1}{2}$ lb., aloes 4 lb., Venice turps $2\frac{1}{2}$ -5 lb., methylated spirit 35 galls.; or, bleached lac 112 lb., sandarach 6 lb., methylated spirit 25 galls.

Steel Lacquer.—Button lac 112 lb., manila resin 7 lb., medium rosin 4 lb., turmeric 12 lb., methylated spirit, 21 galls.

Negative Varnishes.—Shellac $\frac{1}{2}$ lb., sandarach 1 lb., castor oil 3 oz., methylated spirit, 2 galls.

Cabinetmakers' Varnish.—Pale shellac $\frac{5}{8}$ lb., mastic 7 oz., methylated spirit $\frac{3}{4}$ gall.

Brown Hard Spirit Varnish.—Button lac 84 lb., medium rosin 84 lb., methylated spirit 28 galls.

French Polish.—Orange shellac 76 lb., manila resin 10 lb., pale French rosin 10 lb., methylated spirit 50 galls.

Before applying the polish the wood should be made to absorb a little linseed oil and the excess removed by flannel. The varnish is applied with a folded linen cloth impregnated with the polish. It is rubbed softly on the wood until the pores are filled. If the varnish sticks or becomes tacky, a little olive oil is applied by the fingers on the folded linen cloth. The finish is obtained by pouring

a little alcohol on a piece of linen and rubbing the varnished surface until it takes a fine polish. For first-class work polishing with a shellac varnish takes several weeks; *e.g.* pianos in mahogany require at least five times polishing and an interval of time must be allowed, otherwise the polished film dries too hard. It is for this reason that oil varnishes are now in demand for such work (p. 235).

Bookbinders' Varnish.—Garnet lac 118 lb., methylated spirit 10 galls., Venice turps 7 lb., aniline spirit-black $1\frac{1}{2}$ lb., chrysoidine 2 oz. Another variety has the following composition: Button lac 112 lb., sandarach 3 lb., methylated spirit 10 galls.

Many spirit-soluble aniline colours are used which are selected for permanence to light. It is evident that the properties of the shellac are modified by the addition of other resins, *e.g.* manila, sandarach, mastic, Venice turpentine, and benzoin; for each requirement there will be a special formula. The quality of the ingredients varies greatly, so that the formulae are liable to modification. The price is also an important factor, and modifications by the introduction of cheaper resins are much encouraged. The formulae are craftsmen's secrets, and those given above must not be taken too literally, as they give a guide only as to the broad character of the components. In the case of cold lacquers, where evaporation has to be controlled, the addition of amyl acetate and fusel oil are usual, but for decorative bedstead work the competition by lacquers of the Bakelite type has reduced the demand except for very pale varieties.

The application of shellac varnishes may be by brush or spray. In some cases the metal to which the varnish is to be applied is pre-heated, so that the evaporation is accelerated, and by careful brushing a thicker coating is obtained.

Water-soluble shellac solutions are often employed in hat manufacture and for other purposes. The method of obtaining such solution is illustrated by the details of a patent specification claimed by T. Mackenzie.²

Twenty lb. shellac are boiled with 4 lb. sodium carbonate or borax, with or without the addition of rosin, linseed oil, or other gums or oils. A solution of 6 lb. of common salt is added, and then 3 lb. more borax or sodium carbonate are added and the boiling continued for two hours. The solution is reduced to the required consistency by the addition of cold water.

Imported shellac contains more or less wax which must be removed before coloured lacquers can be prepared. A simple method is to heat shellac and borax (10 : 3) with water so that the solution can be easily filtered through linen. On cooling, the impurities settle out and on the surface floats the wax together with any undissolved shellac. The wax is removed, purified by digestion with a boiling soda solution, and is used in polishes and wood stains, etc. The shellac is precipitated from the aqueous solution by treatment with an acid.

Bleached Shellac.—To bleach shellac, it is dissolved in soda and treated with a hypochlorite solution prepared from bleaching

powder and soda, until the desired bleaching is obtained. The solution is treated with acid, filtered immediately, washed with water melted under hot water, kneaded into plaits, and finally dried. By long standing in air shellac loses its solubility in spirit and in borax solution, but not its solubility in soda to the same degree. It can be dissolved in soda, precipitated, and washed, when it will be found to have recovered its solubility, but more borax would be required to dissolve it.³

The loss in weight on bleaching is about 4 per cent; the product is white and rather brittle. Bleached shellac gradually deteriorates in air and in light, becoming insoluble in alcohol and alkalies. If a spirit solution of shellac be turbid, it can be clarified by shaking with a few drops of a solution of hypochlorite, if the turbidity be due to the solvent spirit; whereas if water be the cause, a few grains of solid alkali will be sufficient to clarify the liquid. Mechanical impurities can be removed by filtration through kieselguhr.

Water solutions of shellac are employed in the manufacture of various water-resisting preparations. For example, inks (black or coloured) become fast to water only on the addition of shellac. Both bleached and unbleached shellac are used in borax solution, but not in soda solution.

Shellac Varnish.—The British Standard Specification for Aircraft Material for a shellac varnish⁴ requires that the varnish shall consist essentially of a solution of unadulterated unbleached shellac in industrial spirit and shall contain no added dye. It shall be of such consistency that it will work well under the brush. The film produced by application of the varnish to a glass plate and allowed to dry in a nearly vertical position for four hours at 70° F. (21° C.) shall be bright and free from tackiness. The content of dissolved shellac shall not be less than 25 per cent by weight, when determined by evaporation to dryness on a water bath of a weighed quantity of the clear liquid obtained after the varnish has been allowed to stand for eighteen hours at a temperature of 25° C. (77° F.). Not more than the usual light flocculent precipitate shall separate out when the varnish is kept in a warm place as described above. The iodine value of the solid residue obtained above shall not exceed 32 per cent when determined by the method described in Appendix 1.

The residue from the evaporation test shall give no reaction for rosin when tested by the Liebermann-Storch test. The solid residue previously mentioned obtained by evaporation of the shellac solution shall contain not more than 10 per cent by weight of material soluble in benzene, the estimation being carried out as described in Appendix 2. The amount of ash shall not exceed 0.3 per cent by weight.

Appendix I. Method of Determination of the Iodine Value of the Residue.—0.15 to 0.2 gram of the solid residue shall be placed in a 300 c.c. well-stoppered flask and shall be dissolved by gently warming with 20 c.c. of 99 per cent glacial acetic acid (m.p. 14.8° C.). A slight residue of wax may be ignored. When

dissolution is apparently complete, 10 c.c. of pure chloroform shall be added and the mixture cooled to 70° F. (21° C.). 25 c.c. of Wijs' iodine monochloride solution shall be added and the flask shall be left in the dark for one hour at 70° F. (21° C.). 20 c.c. of a 10 per cent solution of potassium iodide shall be added and the excess of iodine titrated with N/10 sodium thiosulphate. A blank experiment shall be carried out with all the reagents in the same manner and the percentage of iodine absorbed calculated. When rosin or other resins are suspected the quantity of solid used in the test should be kept near to 0.15 gram.

Appendix 2. Method of Determination of Solubility in Benzene.—About 1 gram of the solid residue above mentioned is powdered and added to 100 c.c. of crystallisable benzene. The mixture is heated to about 158° F. (70° C.) for one hour with frequent shaking, after which it is cooled in water at a temperature of about 44° F. (7° C.) for two hours. The clear benzene is decanted, and the residue washed twice with benzene, dried, and weighed.

The above evidently refers to a high-quality shellac varnish.

Copal Spirit Varnishes.—The softer the copal the more readily does it dissolve in methylated spirit. Manila and Borneo copals yield pale solutions which clarify quickly. The degree of solubility of samples of Manila varies, and many leave a stringy residue. The addition of Venice turpentine, gum thus, or elemi gives elasticity to the film. It is wise to dissolve the oleoresin in the spirit and to use that solution to dissolve the copal. The solubility of the harder varieties of copal may be improved by previous fusing, but this causes a darkening of the resin. The fused copals are soluble in turpentine. Other solvents may be used with methylated spirit, e.g. acetone and oil of lavender, but it must be remembered that the less volatile solvent ought to be as good as or a better solvent than methylated spirit, otherwise defects will be observed when the film dries. The addition of castor oil or linseed oil acids improves the elasticity; moreover, linseed oil acids are good solvents for fused and unfused copal. Terpeneol has been suggested as a solvent for the harder varieties of copal, the solution being subsequently diluted with turpentine or methylated spirit, but terpeneol dries very slowly and the amount used must be limited. Sandarach, mastic, and rosin are blended with Manila in many varieties of copal spirit varnishes. Examples of a few varieties of copal spirit varnishes are given below:

White Label Varnish.—20 lb. Manila copal, 10 lb. rosin, 20 lb. methylated spirit. The mixture is heated on the water bath to dissolve the resin.

Pale Spirit Varnish for Wood.—Spirit copal 75 lb., mastic 13 lb., Venice turps 6 lb., camphor a trace, methylated spirit 100 lb.

Black Copal Spirit Varnish for Leather.—Manila 30 lb., sandarach 19 lb., Venice turps 5 lb., castor oil 5 lb., alcoholic solution of nigrosine 6 lb., methylated spirit 150 lb.

A fused-copal spirit varnish is used by bookbinders, whilst a soft-copal spirit varnish is employed in interior decorative work.

Seed lac and rosin are blended with a spirit copal, as instanced by the following formula: Spirit copal 60 lb., seed lac 36 lb., rosin 25 lb., methylated spirit 400 lb.

Dammar Spirit Varnishes.—These have not the defect of Manila spirit varnishes, in that the films cannot be peeled off from the surface before they are quite dry. Their colour and lustre cause them to be preferred to copal spirit varnishes, but they are less durable, slightly tacky, and are apt to dry superficially, so that the surface shows many wrinkles and furrows on weathering. Dammar varnishes are essentially for indoor work. The surface is somewhat friable, so that if the varnish coat is rubbed with the finger it becomes powdery. Turpentine is the usual solvent for dammar, and dissolves it completely at the ordinary temperature. Venice turpentine may be added to impart greater body and elasticity. About 6 or 7 lb. dammar require one gallon of turpentine, but the proportions vary with the source of the dammar. Batavian dammar dissolves better than the Singapore variety. When dissolved in benzene, dammar gives a clear solution and a quicker drying varnish than when turpentine is used. The solution in turpentine is more or less milky, owing to incomplete solution, and on standing a soft white deposit separates. A good negative varnish for proofs on paper may be obtained by dissolving 8 parts dammar in 90 parts benzene and 10 parts methylated spirit. A crystal varnish for paper is prepared by dissolving dammar in its own weight of turpentine and thinning the solution to the desired consistency by the addition of more turpentine. It is also used in making varnishes for coach- and cabinetmakers and for pictures. Its preference lies in the paleness of its solutions compared with those of copal, but if heat be used in the manufacture the varnishes will be coloured. Dammar varnishes may be used for interior decoration and for objects that are not much handled. The drawback to crystal varnish is the slight stickiness of its surface. The addition of rosin gives an inferior variety of crystal varnish. The use of black dammar (p. 126) is small, but occasionally it is used to darken copal oil varnishes when required.

Mastic Varnishes.—Mastic varnishes are highly esteemed for oil paintings, water-colour pictures, and as a paper varnish, but the comparatively high price of the resin makes them expensive. Alcohol dissolves 90 per cent of mastic, but the addition of a small quantity of turpentine will clarify the solution. One pound of mastic dissolves in $1\frac{1}{2}$ lb. turpentine at the ordinary temperature. Other resins, e.g. sandarach, dammar, and rosin, are often blended with mastic.

Fine Mastic.—Mastic 30 lb., rosin W.W. 20 lb., dammar 30 lb., turpentine 10 galls.

Finest Mastic Varnish.—Mastic 6 lb., turpentine 1 gall.

Common Mastic Varnish.—Mastic 10 lb., rosin W.W. 35 lb., dammar 20 lb., turpentine 10 galls.

Mastic varnishes are used for toys and turned articles and for cardboard. If the turpentine solution be mixed with linseed oil

it yields "megilp," which owing to its ease of working is often used as a vehicle by artists in oils, but it possesses several serious faults which make its use undesirable.

It may be noted that when a resin is partially soluble in a liquid, complete solution may be obtained by adding another resin either in the dry state or by dissolving it in the same or another solvent and then mixing the solutions. Rosin is valuable in this respect, and reference to this property has been made under shellac. Venice turpentine, Burgundy pitch, and elemi are also useful, besides imparting elasticity to the varnish films. Such factors make the formulæ of spirit varnishes varied and unsystematic. The special requirements have to be satisfied by alteration of the proportions of the components, which may vary with the consignments of the raw materials, especially as these are bought on the results of the rough tests available to the user.

Sandarach Spirit Varnishes.—Sandarach is used for many purposes because of its hardness, and elasticity is imparted to the varnish film by the addition of soft spirit-soluble resins; *e.g.* elemi, Venice turpentine, mastic, and copaiba balsam, etc. Brown hard and white hard spirit varnishes may be made containing sandarach blended with other resins; *e.g.* white hard spirit varnish: sandarach 2½ lb., gum thus 1 lb., alcohol 1 gall.; or, gum sandarach 2 lb., methylated spirit 1 gall., mastic ½ lb., elemi 4 oz. These varnishes dry to hard lustrous coatings.

Bookbinders' varnish, paper varnish, and negative varnish may all contain sandarach blended with other resins to give the desired hardness and elasticity. A varnish for violins and other musical instruments of wood and for inlaid and panel work may be made by dissolving 1 lb. sandarach, ½ lb. mastic, 2 lb. best white rosin, 3 lb. gum benzine in one gallon of alcohol. One flowing coat is required to produce a mirror-like surface (*vide* p. 235). The price of the resins will largely decide their amount in a varnish. Generally, spirit varnishes are replaced as much as possible by oil varnishes, which are cheaper and more durable, but slower drying. For special purposes sandarach varnishes are still required, but their use is restricted to inside work.

Gum Benzoin is a subsidiary component of spirit varnishes, and is added to confer elasticity on other spirit resins and to preserve surface smoothness of the film.

Rosin Spirit Varnishes are rarely used alone, as they give films of poor quality.

Cellulose Ester Varnishes.—The development of the industry of soluble cellulose has made great strides in the artificial silk industry, in the widespread popularity of the cinema, and in the use of cellulose acetate and nitrate for aeroplane dopes.

Nitrocellulose Varnishes.—The collodion of the *British Pharmacopœia* consists of pyroxilin or cellulose nitrate, $C_{12}H_{21}O_4(OH)(NO_2)_3$, dissolved in a mixture of three parts of ether and one of alcohol. The emulsoid solution is a viscous colourless liquid which on evaporation dries to a brittle film. The film is often opaque,

owing to condensed water deposited from the air during the rapid evaporation of the volatile solvent, and consequently causing a sufficient lowering of temperature. The brittleness of collodion is modified by the addition of plasticising agents; e.g. castor oil and Canada balsam in flexible collodion, or collodion flexile, B.P.

As in spirit varnishes previously described, the properties are capable of adaptation to special requirements. The rate of evaporation, inflammability, and tendency to dry to an opaque film, can be modified by variation in the nature and proportions of the solvents, some of which are true solvents, others non-solvents. Cellulose trinitrate (gun-cotton) is insoluble in a mixture of ether and alcohol. Lower nitrates of cellulose down to dinitrocellulose are also employed as a basis of cellulose nitrate varnishes.

Zapon is a colourless liquid consisting of a low nitrated cotton dissolved in amyl acetate, or a blend of solvents and non-solvents, including amyl alcohol, white spirit, etc. As an adhesive coating it is often blended with shellac. A colourless Zapon solution must dry on polished metal, e.g. brass, to give a transparent film showing no discoloration after several days' application. The thin film must be removed with difficulty by the finger-nail.

Celluloid Varnishes.—If collodion wool or other nitrocelluloses be mixed with camphor and heated under pressure at 120° C., celluloid is formed. Celluloid requires the same solvents as collodion, and yields a colourless varnish which may be coloured with aniline dyes, like all spirit varnishes. The addition of castor oil or a suitable vegetable oil renders the coatings more elastic and more adherent. They are tougher than collodion varnishes, and may be applied in thicker coats, e.g. up to $\frac{1}{4}$ in. thick. The films are adherent, lustrous, waterproof, but very inflammable. Pigments and carbon black may be used to give coloured varnishes of high lustre (*black leather varnishes*).

Dipping Celluloid Lacquer.—Celluloid 6 lb., amyl acetate 50 lb., acetone 4 lb.

Brushing Celluloid Lacquer.—Celluloid, 9 parts; amyl acetate, 45 parts; acetone, 15 parts; methylated spirit, 31 parts.

Black Celluloid Varnish.—Celluloid 90 parts, methylated spirit 150 parts, amyl alcohol 200 parts, carbon black 43 parts, nigrosine 12.5 parts.

Cellulose Acetate Varnishes.—These varnishes have the distinctive character of possessing relative non-inflammability, and moreover, when applied to stretched linen fabrics, have the property of very considerably increasing the tautness of the latter. Although it was considered that commercially acceptable cellulose acetate should approximate to a triacetate and be soluble in chloroform, Dreyfus has shown that little real value is attached to the acetic acid content of a cellulose of primary esterification, and that the properties of the finished product are modifiable in numerous ways by manipulative skill in the acetylation.⁵

It must be understood that the quality of cellulose acetate required in the manufacture of dope for the coating of aeroplane

wings is quite different from that used for the manufacture of artificial filaments, photographic films, and celluloid. In general, it is a fact that the preparation of cellulose acetate intended for films is more exacting than for dope. In the former case the elements of high viscosity, together with clarity and strength of film, are essential features; whereas, in the preparation of dope these properties are of secondary importance compared with those of high solubility and the power of inducing tautness in stretched linen fabrics. As the viscosity increases, the strength of the film and its elasticity show corresponding improvement. If a low viscosity acetate is used, the film will be brittle and of low tenacity. The qualities of the acetates are largely influenced by the conditions of acetylation. The conditions of manufacture of all cellulose esters require careful control to produce mixings of constant viscosity and flow. For an account of the commercial development of the manufacture of cellulose acetate, see a paper by E. C. Worden.⁶

Such cellulose preparations, nitrate or acetate, may be used as the base for metal finishes and, when mixed with aluminium or zinc powder, form rapid-drying primers for metal. Mixed with pigments they dry to form flat washable surfaces, and may be used as substitutes for shellac in some kinds of work. They may be applied by means of a spray or brush, and the film will resist baking at a low temperature. Cellulose nitrate lacquers can be used as primers for certain types of cement floors before painting, and have the effect of preventing waterproofing greases, etc., in the cement acting on the enamel applied subsequently. A cellulose nitrate coating will prevent a metallic priming coat from acting on or being discoloured by a finishing oil-varnish coating. Cellulose lacquer films do not possess the durability of those composed of an oil varnish.⁷

Aeroplane Dopes.—Aeroplane dopes may be looked on as priming coats of soluble cellulose applied on linen for protective purposes. They produce increased tautness of the fabric, but the finishing coat of an oil varnish is recommended for waterproofing. Protection of the linen from ultra-violet rays is produced by incorporating suitable pigments; *e.g.* yellow ochre, ultramarine, and zinc oxide (11 : 5 : 10). Aeroplane dopes may be on a cellulose nitrate or acetate basis. During the war cellulose acetate was preferred to the nitrate, although some maintain that the latter gives more satisfactory results in spite of its inflammability. A variety of dope formulae on a cellulose acetate basis have been put forward. These differ in the proportions of solvents and diluents. A British cellulose acetate dope may contain: cellulose acetate 85 lb., triphenyl phosphate 15 lb., benzyl alcohol 2 galls., acetone 22½ galls., methyl acetone 38½ galls., ethyl alcohol 11 galls., benzol 26½ galls. Benzol, ethyl alcohol, and benzyl alcohol are diluents, and are mixed with the cellulose acetate before the addition of the solvents, acetone and methyl acetone. The standard French aeroplane dope consists of—For summer use: cellulose acetate

80 parts, benzyl alcohol or phenol 40 parts, solvents and diluents 890 parts; for winter use the benzyl alcohol or phenol and the solvents and diluents are reduced by 10 parts each respectively. The solvents and diluents consist of methyl acetone, methyl acetate, or ethyl formate 410 parts, benzol 250 parts, alcohol 220-230 parts. Ethyl acetate, butyl formate, or methylethyl ketone may replace the solvents to the extent of 33 per cent. The order of mixing is essentially the same as in the British preparation. One gallon of dope covers 7 yds. of wing surface when applied in the form of three coats. Excess of benzol produces brittle films, while excess of alcohol gives films of low tensile strength.⁸ A dope formula from an American source is as follows: 7.9 oz. cellulose acetate; 1 oz. triphenyl phosphate; 1 gallon of solvents and diluents, of which 60 per cent is methyl acetate, methyl ketone 10 per cent, acetone 10 per cent, benzol 15 per cent, and diacetone alcohol 5 per cent. Small quantities of benzyl acetate, benzyl alcohol, benzyl benzoate, or urea are added. These increase the flexibility of the film, and are not usually required when the dopes are used for other purposes.

Nitro-dope coverings contain essentially the same solvents and diluents as in the acetate dopes, but with the addition of castor oil. The nitrocellulose must be a low nitrated cotton of good quality, and must comply with the Abel heat test for stability. It must be completely soluble in butyl acetate, and the viscosity of a 5 per cent solution, as measured by the Ostwald viscometer, is to be between 45 and 50 at 25° C. (glycerol = 100).

Typical formulae for nitro-dope coverings as issued by the British Engineering Standards Association as British Standard Specifications for Aircraft Material are given below (D. 103, Nov. 1920):

Nitro-Dope Coverings.	Transparent Covering, V. 114.	Protective Covering, P.C. 10.	Nivo Covering.	Matt Black Covering, V. Bl. 4.
Nitrocellulose syrup	260 lb.	232 lb.	260 lb.	260 lb.
Butyl or amyl acetate	18½ galls.	15 galls.	15 galls.	15 galls.
Alcohol	22½ "	15 "	15 "	15 "
Benzol	22½ "	15 "	15 "	15 "
Acetone	" "	20 "	20 "	20 "
Castor oil	77 lb.	52 lb.	75 lb.	31 lb.
Pigment	" "	150 "	119 "	39 "
Total	97 galls.	95 galls.	102 galls.	96 galls.

[TABLE

	Protective Covering, P.C. 12.	Aluminium Covering, V. 84.
Nitrocellulose syrup	260 lb.	260 lb.
Butyl or amyl acetate	30 galls.	20 galls.
Alcohol	7½ "	12 "
Benzol	7½ "	12 "
Methyl ethyl ketone	20 "	22 "
Castor oil	42½ lb.	25 lb.
Pigment	92½ "	150 "
Total	97 galls.	100 galls.

IDENTIFICATION COLOURS

	Red. V.R. 3.	White. V.W. 3.	Blue. V.R. 2.
Nitrocellulose syrup	260 lb.	279 lb.	260 lb.
Butyl or amyl acetate	20 galls.	20 galls.	20 galls.
Alcohol	20 "	20 "	20 "
Benzol	15 "	15 "	15 "
Acetone	15 "	15 "	15 "
Castor oil	40 lb.	50 lb.	52 lb.
Pigment	110 "	250 "	140 "
Total	102 galls.	107 galls.	106 galls.

The pigments incorporated in the nitro-dope coverings are as follows: In P.C. 10, yellow ochre and carbon black are blended to match a standard. For the "Nivo" covering yellow ochre, lithopone and ultramarine blue are matched to a standard. For matt black covering gas-carbon black is used. For the identification colours the red consists of a dye prepared from the sodium salt of the product obtained by diazotising 2-naphthylamine 1-sulphonic acid and coupling with β -naphthol, struck on barium sulphate. The pigment for the white colour is zinc oxide, whilst for the blue a mixture of ultramarine blue and zinc oxide is used. For the details of manufacture of the nitro-dope coverings reference must be made to the published specification. It is advisable to mention that the nitrocellulose is dissolved in the solvent first and the diluents are added later, in contrast to the order observed in the manufacture of cellulose acetate dope.

For the properties of these mixings reference again must be made to the specification given above.

The protective powers of cellulose nitrate dope are said to be greatly improved by the addition of 5.7 per cent casein, or "treated" tung oil, which makes the film hard, and reduces the rate of evaporation.

A large number of patents have been issued for improvements in the properties of dopes for aeroplanes. A few may be quoted :

A. J. Barr and H. Lazell⁹ claim to prepare a dope which tautens and is waterproof by adding to a cellulose dope a mixture of pigments consisting of yellow ochre, ultramarine, and zinc oxide. Reduced visibility, as well as prevention of excessive darkening, is obtained by the addition of aluminium powder; e.g. 300 galls. cellulose acetate dope, 10 lb. mixed pigments, 5 lb. aluminium powder.

The British Aeroplane Varnish Company¹⁰ claim that the addition of beeswax and paraffin wax, having a total weight equal to that of the cellulose ester or celluloid of the dope, minimises the variability in the tension of the aircraft fabric to which it is applied and improves the resistance to water.

Formerly chlorohydrocarbons, tetrachlorethane, were employed among the solvents, but the vapours proved toxic, and in 1916 their use was prohibited. The British Emaillite Co. and J. N. Goldsmith¹¹ claim to obtain satisfactory results by replacing the chlorohydrocarbons by other solvents with the addition of triacetin or acetanilide in the proportion of 5-10 per cent on the weight of the cellulose ester used.

Titanine, Ltd., and Bowles¹² claim that aeroplane dope with the addition of boric acid or an equivalent amount of borate to give 0.2 per cent free boric acid can be stored in a galvanised iron drum for several months with only a negligible change in viscosity.

D. H. Sutherland and Wallpaper Manufacturers, Ltd.,¹³ claim that the use of "borated" benzol (boric acid 10 per cent, benzol 90 per cent), as an addition to varnishes containing acetylcellulose or nitrocellulose, permits the use of a larger percentage of benzol without causing precipitation of the cellulose. The addition is claimed to replace triphenylphosphate as a fireproofing agent, to retard drying, and to reduce the viscosity of the varnish.

Herzog, Hildesheimer, and Medicus¹⁴ give a summary of the nature of substances to be added to nitrocellulose solutions to produce pliability of the films.

The detailed treatment of aeroplane dope shows how the properties of cellulose derivatives are influenced in solution by the presence of varying solvents and diluents. The properties of the soluble cellulose are also strongly modified by variations in the conditions of manufacture, as was shown by Dreyfus: A chemical analysis of cellulose acetate is no criterion as to its suitability as a dope. The statements which have been made in connection with aeroplane dope apply also to the cellulose and celluloid varnishes used for other purposes.

Black Leather Varnishes.—Black leather varnishes may be made on a spirit basis, the ingredients consisting of shellac, sandarach, a spirit copal with turpentine and Venice turpentine, using lamp-black as the black pigment. A black harness leather varnish may be made by mixing and heating to boiling 24 parts shellac, 4 parts sandarach, 4 parts elemi, 16 parts Venice turps, and 12 parts

turpentine. After cooling, 1000 parts of alcohol are added, followed by 40 parts lampblack, and the whole is well stirred. Similarly a black varnish for belts may be made comprising 100 parts shellac, 20 parts pine resin, 50 parts Venice turps, 40 parts turpentine, 100 parts alcohol, and 40 parts lampblack. These varnishes dry in the air and are elastic even when the leather is bent.

The use of nitrocellulose solutions for patent and enamelled leather has become widespread, and now largely displaces the older linseed oil varnishes. It is not advisable nowadays for the leather dresser to make his own dope finishes, as they require careful and special preparation. Three coats are applied, bottom, middle, and top coats. The first coating is applied with a fairly stiff brush and worked well into the leather. A high temperature is not required, 60°-100° F. being suitable. The effect of drying at a higher temperature is to reduce the adhesion of the film to the leather. The second coat is to build up colour and to correct inequalities of the first coating. The varnish is applied with a well-soaked swab attached to a suitable handle. The top coat is applied in a similar manner and spread thinly and evenly, so as to leave no tackiness, and is dried under the same conditions. Embossing and printing must be done with a special machine. For further details reference must be made to text-books on practical leather manufacture.¹⁵

Specifications for Resins and Shellac for Spirit Varnishes.—Under Shellac Varnish (p. 289) a specification of the Aircraft Section of the British Engineering Standards Association has been given *in extenso*. Attempts have been made to standardise a number of spirit-soluble resins for the purposes of purchasing specifications, and it may be advisable to consider them carefully. W. B. Parker¹⁶ states that the specifications which have been published do not correlate the true facts concerning these materials with business requirements and general experience. Merchants and brokers do not welcome the introduction of standards of such substances as resins. To quote from Sir A. Denny's address published in the Annual Report of the British Engineering Standards Association, 1922: "Standardisation is reconstruction in the very highest form. It may not lead directly to making large profits, but it will certainly lead to the maintenance of our industries, because it will enable us to compete with the best that is found abroad; it will cheapen manufacture as well as increase the volume of trade and the prosperity of this country." Such a statement is applicable to standardisation of resins by specification, if it can be shown satisfactorily that their characteristics are definitely connected with requirements. The difficulty in the case of resins is that their chemical composition and properties appear to play a less important rôle than in the consideration of oils and thinners. The difficulties in specifications for gelatine may be recalled, and the same will apply to resins. Parker has enumerated in detail the chemical and physical characteristics which he considers are of importance. All will agree that the acid value, and to a less degree the iodine value,

specific gravity, solubility, hardness, colour, ash content, moisture, and boldness of size are characteristics which differentiate quality of material. Is it always safe to buy on such figures? Is it always certain that lustre, hardness, elasticity, and durability of a varnish film are fixed by certain numerical values of such characteristics? Many of the resins are fused, and the properties of the "run" resins depend on works conditions, which are varied. The properties of the resin films are those of depolymerised substances which are incorporated in oil and thinner, and whose degree of dispersion is dependent on works conditions. Each factory has its own mode of testing according to its requirements, and a standard specification for copals must be accepted with reserve. It has been pointed out that the loss in weight of running of a copal has no connection with the acid or iodine value. Nevertheless, in spirit varnishes there is scope for standardisation of the resin components, but much more investigation is required before most spirit resins can be satisfactorily dealt with. Parker gives detailed specifications for the varieties of lac (shellac, button lac, garnet lac), dammar, kauri, and manila, and for the details the reader must be referred to the original paper. The whole subject is one which would come within the sphere of work of a Research Association, which is so much wanted in the paint and varnish industry, if real progress is to be gained. It is not so much a popularity of the methods which are already known which is required, but a fuller knowledge of the principles on which the methods are based.

The Analysis of Spirit Varnishes.—The scheme of analysis is divided into two sections: (1) The separation and estimation of the solvent; and (2) the examination of the residue after the removal of the solvent.

The Separation and Estimation of the Solvent.—If the solvent be alcohol, distillation and examination of the distillate is carried out by the usual method, and the distillate may be fractionated. If the removal of the solvent be carried out in a current of steam, the volatile solvent insoluble in water will separate and the water-soluble components must be examined separately. For details of the detection and estimation of methyl alcohol, ethyl alcohol, amyl alcohol, amyl acetate, acetone, ether, benzol, chlorohydrocarbons, etc., reference must be made to Allen's *Commercial Organic Analysis*, as well as for the aniline colours in coloured spirit varnishes, which have replaced the vegetable dyes formerly used, because of their greater variety, cheapness, and general stability to light and heat.

The Examination of the Residue.—The examination of the residue, if an oil be present, is the same as in the case of an oil varnish involving separation of oil and resin. If oil be absent, the resins can be detected by special tests, which have been dealt with under the heading of Resins. It has been pointed out that a scheme for the general estimation of resins in a mixture is very imperfect and generally unsatisfactory.

H. Rebs¹⁷ has put forward a scheme for the detection and

separation of the commoner resins. Concentrated acetic acid will dissolve lac, rosin, an oleoresin of turpentine and accroides resin. Very dilute ammonium chloride will dissolve lac, while manila, sandarach, rosin, and accroides are insoluble. Benzine (light petroleum) will dissolve rosin or an oleoresin, but manila, sandarach, lac, and accroides are insoluble in that solvent. In order to separate the different resins qualitatively and quantitatively in a spirit varnish, the solvent is distilled off, the residue is finely powdered and warmed on the water bath with the solvents mentioned above. If lac and rosin be present, the lac will dissolve in very dilute ammonium chloride. Lac may be separated from manila or sandarach, and likewise from rosin, but the separation of sandarach from manila copal is very doubtful. The estimation of dammar admixed with spirit copal or kauri by means of alcohol and chloroform has been put forward by Stewart.¹⁸ The resin is boiled with alcohol, which dissolves the spirit copal and part of the dammar. The residue is extracted with chloroform in a Soxhlet, whereby the remainder of the dammar is dissolved. The amount of the chloroform-soluble extract is a measure of the percentage of dammar. The insolubility of a genuine sample of the particular variety of dammar must be known.

It is evident that the methods of separation of the individual resins in a mixture are by no means satisfactory, and there is need for much investigation in that field.¹⁹ At present the works tests are essentially the most reliable. Elasticity, lustre, hardness, uniformity of film, and, in the case of coloured spirit varnishes, stability to heat and light, are compared against special requirements. On metals the varnish film must be clean and the coating must not have an acidity likely to set up chemical interaction with the metals. Determination of acidity, behaviour on drying, flow, colour, and specific gravity are compared with corresponding values of the standard sample.

If the spirit varnish contain nitrocellulose, celluloid, or cellulose acetate, the residue after the removal of the solvents must be examined by special tests. Treatment with a dilute solution of diphenylamine in concentrated sulphuric acid will give a blue coloration in the presence of nitrocellulose. Nitrocellulose may be estimated in the residue by measuring the volume of nitric oxide evolved by the action of ferrous chloride and hydrochloric acid at 100° C., whereby the nitro-group of the nitrocellulose is reduced to nitric oxide.

Celluloid may be detected by the identification of the incorporated camphor, which can be removed by ether or by methyl alcohol, in which the nitrocellulose is insoluble.

For the detection of cellulose acetate, gentle heating with concentrated sulphuric acid and a little alcohol will give amyl acetate.

For the identification of the cellulose component the original residue may be boiled with hydrochloric acid (s.g. 1.10), neutralised, and tested for the sugars with Fehling's solution. The cellulose in

nitrocellulose and celluloid can likewise be detected by the production of reducing sugars on hydrolysis.

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CHAPTER XVI

INSULATING VARNISHES

VARNISHES are valuable insulating materials, owing to the high dielectric constants of resins, vegetable oils, and pitches. The following table gives the specific inductive capacity of a number of insulating materials :

Asphaltum	2.68	(Pirani).
Glass, Crown . . .	5—7	} (Physical and Chemical Constants).
" Flint	7—10	
Paraffin	2—2.3	
Rosin	1.8—2.6	
Shellac	3—3.7	
Porcelain	4.4—6.8	
Paper	2—2.5	
Mica	5—7.7	
Sulphur	3.6—4.3	
Castor oil	4.6—4.8	
Turpentine	2.2—2.3	} (Elect. Test. Laboratories, N.Y.).
Petroleum	2.0—2.2	
Bakelite	5.7—6.8	

The solution of gum and oil in suitable thinners is allowed to impregnate other insulating materials and, after volatilisation of the solvent, a film of non-conducting material is left with good moisture-resisting properties. The moisture-resisting properties of a varnish deserve careful consideration. Those engaged in the construction of electric machinery know the great hygroscopic power of most of the principal materials employed, cotton, paper, etc. They know also that moisture is the most dangerous factor to be considered in problems of insulation. If the film be sufficiently elastic to bear strain under rise of temperature without becoming brittle or fusing, the surface coating will remain intact for a long period. Another factor of importance is the penetrating power of the varnish into cotton or paper, whereby the dried material becomes cemented by the impregnating substance. It is necessary to dry carefully cotton and paper used in windings or as insulators, previous to the application of the varnish coating. " "

The functions of insulating varnishes are :

- (1) To provide a waterproof coating with sufficient elasticity to withstand the movement between parts produced either by rotation or by magnetic or electric forces.

(2) To increase the insulating properties of the impregnated material.

(3) To protect the parts from the action of oils and acids.

(4) To prevent excessive rise in temperature through their relatively high thermal conductivity.

Classification of Insulating Varnishes.—The description of insulating varnishes has not received proper attention in many English varnish text-books, although some varnish firms issue pamphlets describing the properties and uses of their preparations. It is generally left to the electrical engineer to put forward his requirements and to state the conditions under which the materials are used. A short description of insulating varnishes is given in Morrell and de Waele's *Rubber, Resins, Paints, and Varnishes* (1921), which is based largely on Fleming and Johnson's *Insulation and Designs of Electrical Windings* (1913). A more recent publication is *Les Vernis isolants en électrotechnique* (A. R. Matthis, 1921), which gives full details as to their composition, properties, and modes of application. An attempt will be made to indicate the classes of varnishes suitable for different systems of insulation, without going into details of their composition. To the electrician a breakdown due to defective insulation is costly, and leakage of current makes economical and safe working impossible. The varnish which will suffice for all purposes does not exist, and the only way is to manufacture a series of products, each specially designed to meet requirements.

Fleming and Johnson¹ classify insulating varnishes as follows :

(1) Varnishes for impregnating windings ; (2) varnishes for treating paper and fabrics ; (3) cementing varnishes ; (4) finishing varnishes.

Varnishes for Impregnating Windings.—These varnishes are used to fill the coverings of windings, thereby increasing their insulating value and rendering them moisture-resisting. They are required to withstand the action of hot mineral oil, which is essential in the case of oil immersed windings. The varnish films should be sufficiently flexible to withstand mechanical stress and also the expansion or contraction of the windings, and to retain their flexibility for a long period. There must be no corrosive action on the copper conductor or destruction of the fibrous insulation coverings by any component of the varnish. They should be free from organic acids which tend to become active during the process of oxidation of the varnish, especially on stoving. The surface acidity of the film, which is a result of the drying process, must be reduced to a minimum, and the perfect smoothness of the film must be maintained so as to avoid condensation of water. The corrosive action of the varnish on copper is not serious, except in the case of fine windings, 0.02 in. diameter and smaller, but it is advisable to test the varnish beforehand by covering a plate of copper with a linen band, impregnating it with the varnish, and allowing it to dry. After three days' exposure to the air the copper and the linen ought not to have acquired a green colour. Any corrosive action appears to

cease when the varnish becomes dry, since the green discoloration often noticed on cotton-covered windings, impregnated with resin-linseed-oil varnishes, especially those containing turpentine, occurs only during the drying process. When once the varnishes have hardened, no further action is observed, provided that the cotton has been properly dried previous to insulation.

The conditions governing the production of chemical action in high-voltage windings are given by Fleming and Johnson,² and may be summarised as follows: Chemical action occurs only where air pockets are present, due to lack of care in construction of the windings, and then only when the voltage across them is high enough to produce discharge. The action of the products of an 'air-gap' discharge is one of oxidation, and the effect produced on oils and gums is to yield organic acids, whereas asphaltums are attacked only to a limited extent and paraffin wax remains unchanged. The organic acids act strongly, disintegrating on the varnish material. The production of nitric acid is not essential for deterioration of insulation, although when it is produced the action is greatly accelerated. For the range of voltages in use and with any of the methods of winding and insulating commonly employed, failure of machines from chemical action is not to be expected, when the average stress across slot insulation is less than 35 volts per mil. Generally, the electric stresses are really very low, and in field coils are much lower than the above figure. A much higher average stress than 35 volts per mil. of slot insulation is safe when the size and number of the conductors permit the best method of grouping and insulating to be employed, and when special precautions are observed as to the kind of materials used and the proper filling of the interstices. The green discoloration which frequently occurs on coils of any voltage treated with resin-linseed-oil varnishes should not be confused with the chemical action due to the products of the air-gap discharge, which takes place in high-voltage windings only. Such discoloration is quite harmless with the best makes of varnishes.

Experience has shown that the organic acids are not the main cause of insulation failures.

Matthis³ considers the presence of rubber or vulcanised rubber to be no advantage and the latter a real disadvantage. It would appear that the breakdown voltages of rubber films obtained from solutions of rubber in solvents are low compared with oil varnish films. A certain amount of metallic drier is allowed in air-drying coatings, and of manganese and cobalt in stoving varnishes. The oxidation of a varnish continues slowly even after it is apparently dry, so that the elasticity will slowly decrease, and care must be taken that the amount of drier present is not excessive. An air-drying oil varnish ought to be hard in ten to fifteen hours, and a stoving varnish in twelve to fifteen hours, at a temperature of 100° C., but much depends on works conditions. Pitch varnishes containing linseed oil have a more permanent flexibility, but are less resistant to mineral oil. Resin dissolved in spirit or in a suitable petroleum

thinner separates out on the expulsion of the solvent, but the films lack the flexibility of linseed oil varnishes. Shellac varnishes are more suitable for insulation of low voltage windings, such as instrument coils, where the temperature variation is small and no mechanical stresses have to be considered. The coatings are brittle, and although shellac dries quickly it does not withstand the action of moist air.

The so-called heat-radiating varnishes are comparatively poor insulators, due to the amount of mineral matter employed in their manufacture, and more satisfactory results are obtained by filling the interstices in the windings with solid compounds. The formulæ given below may be considered as typical of oil and pitch insulating varnishes :

Stoving Insulating Varnish.	Stoving Black Insulating Varnish.	Impregnating Compound.
300 parts stand oil	300 parts thick linseed oil	100 parts asphalt.
300 „ China wood oil	100 „ asphaltum pitch	200 „ crude ozokerite.
135 „ hardened rosin	7 „ sulphur	70 „ rosin.
7½ „ manganese dioxide	2 „ litharge	„
600 „ light petroleum	1 „ manganese dioxide	„
	100 „ turps	(Seelligman and Ziecke.)
	400 „ light petroleum	

The varnishes must be clear, neutral, or only slightly acid, and chemically stable to withstand temperatures even up to 200° C. ; they must be unattacked by lubricating oils, resist the action of ozone and salt water, and be unacted on by acid vapours such as may be evolved from accumulators.

The Sterling Varnish Co. recommend the following general tests for viscosity, elasticity, adhesion, penetration, behaviour at high temperatures, heat conductivity, chemical resistance, dielectric rigidity, resistance to water, alkalies, acids, and mineral oils. A few of these requirements may be treated in detail.

Elasticity.—The degree will depend on the requirements, but for impregnating purposes it must be high, and the brittleness test already described (p. 233) will apply. Instead of sheet metal, either linen or paper may be used by bending the coating over a piece of wood of known thickness or a metal wire of known radius. A layer of thick varnish shows less elasticity than one which is thinner, but this depends on the varnish under examination. A film of an elastic varnish on metal is less dependent of the thickness of the layer (p. 265).

Penetration.—A better penetration gives better insulating power and depends on the consistency. The density is related to the penetrating power, because it is often an indication of the dilution by thinners. In all impregnation schemes, it is advisable to provide for an outlet of the imprisoned air in the windings, as well as for suitable passages for the ingress of the insulating material. The degree of penetration may be arrived at by observing the number of layers of cotton-covered wire impregnated by the material after

a period of immersion at a fixed temperature. Another method is to observe the number of sheets of blotting-paper, built up into a pile of known thickness, through which the varnish will penetrate.

Heat Conductivity.—There is a difference of 25 per cent in the temperatures of an unvarnished and varnished cotton-covered wire on the passage of an electric current, so that it is advisable to have as insulating material a good conductor of heat. The heat effect may be compared by measuring the resistance of the insulated and non-insulated coils during the passage of the current or the difference of potential between the extremities.

Breakdown Voltage Test.—The testing as carried out by the National Physical Laboratory is on the lines of impregnating coils of double cotton-covered wire and submitting adjacent layers of the coils to an increasing alternating voltage until the breakdown occurs. The pressure is applied to the coils in steps of 100 volts for periods of one minute, starting at 500 volts. The varnish coating would have been previously stoved at 155° F., 23 in. vacuum, or 240° F. at ordinary pressure.

The coils used are made up with No. 20 double cotton-covered wire, the winding and number of turns being identical in all the coils. They consist of four layers of winding, each approximately 2 in. wide and 4 in. in diameter, wound in close contact on a former and bound together with silk tape in the usual way. The coils are dried in a vacuum before impregnation with the varnish. The results of the tests on the dry coils are scheduled in the following table :

Varnish.	Method of Stoving.	Breakdown Voltages.	Time of With-standing Break-down Voltage.	Mean Breakdown Voltage.
1 . . .	155° F. (Vacuum)	1300 1300 1400	Uncertain	1330
8 . . .	"	1200 1300	"	1270
1 . . .	240° F. (Atmospheric pressure)	1300 1400	10 seconds	
"	"	1400	0 "	1400
"	"	1400	5 "	
8 . . .	"	1200	0 "	
"	"	1300	0 "	1270

Another method of measuring breakdown voltage is by impregnation of cotton or paper by the varnish and subjecting it to an electric tension between two electrodes until a breakdown occurs. The voltage is gradually raised in successive stages of 100 volts per minute. The thickness of the layer is taken, and if the thickness of the cotton or paper is known, the thickness of the varnish films can be obtained. The breakdown voltage is stated for 1 mm. thickness of film. The following table gives the breakdown

voltage of a number of varnishes applied on cotton. The weight of the varnish is known, and the thickness is that of the impregnated cotton. The density or the amount of varnish per cubic mm. is a measure of the actual protecting thickness of the film. The percentage of absorbed moisture was obtained by hanging the strips in a damp atmosphere for one hundred and sixty-eight hours.

On Linen Cotton.	Weight, grams.	Thick- ness, mm.	Density, mgrms. per c.mm.	Breakdown Voltage.	Break- down Voltage per mm.	Per cent Water Absorp- tion (168 hrs.).
Black oil varnish for coils	6.8072	0.3838	0.5728	1000	2,605	2.5
Clear varnish	7.9308	0.3325	0.7532	3800	11,400	7.25
Clear varnish	6.2966	0.3160	0.7079	3983	12,600	6.15
Black finishing var- nish	7.0566	0.382	0.5967	783	2,049	1.8
Cotton	200 (dried)	..	15.6

The pressure test affords no real criterion as to the safety of windings against chemical action, since the stress at which the latter takes place is usually far below that at which disruption of the insulation occurs.

Resistance to Water.—The varnished windings are kept in steam for twenty-four hours or in a moisture-saturated atmosphere for a period of days and then tested for breakdown voltage, which ought to be unchanged.

The Action of Acids.—Immersion in 10 per cent nitric acid or 10 per cent sulphuric acid must show no change in the appearance of the coating.

The Action of Ozone.—This test is of importance as affecting the chemical stability of the material. It may be carried out by subjecting the films to a voltage, 75 per cent of the breakdown value of the film, applied for six hours so that the ozone produced may act on the varnish. At the expiration of that period the coating must be unchanged.

The Action of Lubricating Oil.—The insulated material is subjected to the action of lubricating oil for twelve hours at 150° C., and any alteration in the appearance or softening of the film is noted. It is advisable to carry out a blank test with the lubricating oil heated under the same conditions, so as to observe any change in the appearance of the oil due to action of the varnish on it. Some authorities recommend immersion in mineral oil (s.g. 0.89) at 100° C. for one hundred hours.

The American requirements for insulating varnishes may be summarised as follows:—Insulating varnishes may also be classed as baking oil, air-drying oil, and air-drying spirit varnishes. For coils of armatures or rotating parts the varnish films must have

high dielectric strength and be impermeable to moisture. For stationary parts careful selection is not so vital, though dielectric strength must be high. The suitability of a varnish for insulating purposes is determined by its dielectric strength, an ageing test, and a test on coils; the latter comprises time of drying, measurement of insulation, resistance between parallel conductors under various conditions, the penetration and internal drying properties, and the tendency to discolour when the coils are subjected to heat and moisture. The dielectric strength is determined by dipping a strip of paper, 0.025 mm. thick, in the varnish to be tested and determining the breakdown voltage of the varnish film. The paper is given two dips and is drained in the opposite direction between dips. In the case of a baking varnish the paper is baked between the dips in an electric oven. For an ageing test a piece of the varnished paper is kept at 80° C. until it will break when bent double, and the time of heating required is noted.⁴

Solid Impregnating Compounds.—Solid impregnating compounds on an asphaltum basis have been preferred for field coils and stationary windings. "The impregnation is complete in one operation, the coatings are more chemically inert, are better fillers, and more resistant to moisture. The temperature of impregnation is higher for a "compound" than for a varnish; in fact, it must be as high as possible, whereas with varnishes it is as low as possible. There is a difficulty in the selection of an asphaltum which will impregnate the windings at suitable temperatures and will not ooze out during use. The oxidation and polymerisation of a varnish will give an elastic coating sufficiently hard, and will not soften under the influence of heat, but it is difficult to remove completely the whole of the volatile thinners from the interior of the coil unless precautions are taken to provide suitable outlet passages. The impregnating compounds require no thinners and solidify on cooling, rendering the enclosed parts insensible to vibration. If a machine be overloaded, the impregnating compounds will, unlike varnishes, soften and melt; and if the parts revolve, centrifugal force may cause exposure of parts requiring protection. Generally the asphaltums used soften at 105°-115° C. and do not become appreciably fluid below 150° C. They consist of asphalt, pitch, rosin and copal, run together until water has been expelled. In order to make them mineral-oil resistant a certain amount of sulphur is mixed in.

If the impregnation temperature be too high (above 175° C.) there is danger of carbonising the cotton covering. Impregnating compounds are not much employed in transformer work. Their resistance to lubricating oil is inferior to that of oil varnishes, and it is doubtful whether there is an oil-resisting compound on the market. In the examination of samples it is advisable to select one from the middle of a cask. The fusion temperature may be taken as that at which the first drop falls from the bulb of the thermometer to which a piece of a softened sample has been attached. The penetration power may be arrived at by the same

method as described under Varnishes. The hardness may be measured by observing the depth of penetration of a needle (1 sq. mm. section) under a known weight during a given time and at a fixed temperature. The viscosity can be determined by any torsion viscometer (Doolittle or MacMichael).

The thermal conductivity of "compounds" is greater than that of varnishes, and the temperature in the windings will be lower in coils impregnated with compounds. The resistance to water and acids can be carried out as described under Impregnating Varnishes.

It must be left to the electrician to decide whether he will use an impregnating compound or a varnish, as much depends on the construction of the machine. The mode of testing will be prompted largely by technical requirements, and the engineer will use the methods that he finds most suitable for the conditions to which the machine has to be subjected.

Methods of Application of Insulating Varnishes.—The thickness of the varnish required for impregnation varies with the parts of the machine to be insulated, and the dilution by means of thinners, will vary with the number of layers, dimensions, etc., of wire in the coils. Varnishes possessing the same density need not possess the same consistency, and the viscosity value is of much greater importance. The specific gravity variations are of use only when dealing with the same varnish.

The insulating value of a varnish depends on its penetration, and also on its viscosity. Too thin a varnish gives poor dielectric strength, due to lack of body; too thick a varnish yields poor dielectric strength, due to lack of penetration. The dielectric strength is greatest for minimum increase of thickness, i.e. when the breakdown voltage per unit thickness is the maximum.

The complete drying of the parts to be insulated is of the highest importance, because of the heat developed by alternating electric stresses. If enough water be present to permit of electrolytic decomposition, no varnish can withstand it. Insulating material consists of fibres in which traces of moisture may be enclosed. Under alternating electric strains a "current of displacement" is developed which generates heat. The increase of temperature decreases the dielectric strength of the materials and also ruptures the films of insulators applied. Owing to its hygroscopic nature, cotton holds 5-8 per cent moisture under ordinary conditions. The importance of complete drying is admitted by all, and many breakdowns attributed to varnishes are really due to humidity enclosed in the materials. To expel moisture a temperature of 100°-110° C. is required in a stove suitably ventilated to remove the evolved water-vapour. The use of vacuum stoves avoids the difficulties of preventing absorption of water-vapour, gives economy of working with no deterioration in the materials to be insulated, and renders them more susceptible to impregnation. Cotton thread, although unchanged at 100°-110° C., begins to turn yellow at 175° C., and at 225° C. carbonization becomes marked

and is complete if the cotton be kept at that temperature. Matthis considers that the introduction of a little warmed air during the vacuum drying is of advantage. Impregnation follows the vacuum drying process, and the varnish is drawn into the receptacle automatically. The vacuum ought to be good, *i.e.* 99 per cent, in order to ensure complete removal of moisture. Volatile thinners escaping during impregnation may be collected in a suitable condensing system. The impregnated parts are stoved in well-ventilated stoves to facilitate oxidation, the temperature being measured by pyrometers, which can be read outside the stove. Uniformity of drying is advisable, and the stoves ought not to be opened except for removal of the whole charge. If gas jets are used for heating, it is advisable to have a perforated plate above them so as to distribute the hot air. If the stoves be steam-heated, the pipes should be laid around the sides, and if electricity be used the system of wires should be similarly laid. The time and temperature of stoving depend on the engineer's requirements; *e.g.* 240 F.° at ordinary pressure. If a vacuum stove be used the temperature may be 155° F. with 23 in. vacuum. The stoved layer of insulating coating must not have a tack. When two or more coatings are applied, the windings should be drained from opposite ends so as to make the coating as uniform as possible, and the first must be dried thoroughly before the application of the second. In dealing with "compounds" the windings to be impregnated are dried in a vacuum chamber. The compound is melted in a steam-coil-heated tank and introduced into the vacuum chamber by opening a valve in the connecting pipe, the atmospheric pressure forcing the compounds out of the melting tank into the vacuum chamber. The windings are subjected to an air pressure of 80 lb. to the square inch, so as to complete the impregnation. The remainder of the compound after the impregnation generally requires addition of a suitable blender to restore the original fluidity.

Fig. 42 is a diagrammatic representation of the plant used in the process.

Varnishes for Impregnating Papers and Fibres.—The requirements are good flow, good penetration, high moisture-resisting power, and great flexibility. It is of importance that the physical properties of the coating should be permanent under working conditions, so that it does not become brittle. Freedom from mineral acids is not of importance, provided that the paper or fibre is unattacked. The varnish coating after stoving at 100° C. must give a smooth elastic surface with a thickness of about 0.002 in., and must be unaltered by hot oil. The insulated fabrics or paper are tested according to the scheme already described.

Varnishes for Cementing Purposes.—These varnishes are used in the building up of mica sheets and in the preparation of mica cloth. Spirit varnishes, shellac with or without rosin, or spirit-soluble copal in methylated spirit, may be used. The addition of a little castor oil confers elasticity. The varnishes dry without

oxidation, but their use is restricted by temperature limitations. Generally they are made up when required; *e.g.* in the proportions of 1:1, coloured with aniline colours. The air-dried layer must not be sticky. Varnishes for cementing purposes depend largely on the use to which the cemented mica is put. The material used

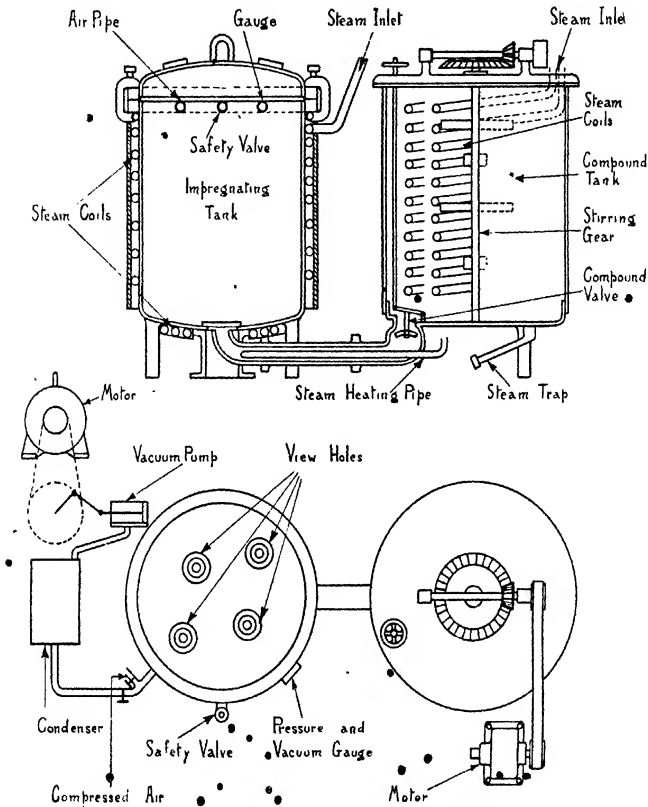


FIG. 42.—Impregnation plant (Fleming and Johnson).

in a commutator needs to differ considerably from a cemented layer used for mere insulating purposes. They find employment in the preparation of insulating tubes and cylinders of papers and mica.

Varnishes for Finishing Purposes.—These varnishes are used to give a smooth coating to the coils and windings, which will prevent

dust and dirt accumulating on the surface. They must be air-drying or low-stoving, and be able to resist lubricating oil and sulphuric acid. Shellac, with or without rosin, and pitch varnishes give a smooth surface, but are apt to be brittle, unless some elastic oil component is present (castor oil in shellac and thick linseed oil incorporated with pitch). The varnishes are sprayed, or brushed on. Provided the windings are protected by smooth tape, the impregnating varnish is often sufficient, although the surface must be hand brushed, which adds to the cost of production.

Varnishes for Transformers.—For dry transformers (cooled naturally) micanite insulation is employed, but micanite sheets can only be used in small oil-insulated transformers, because the material causes overheating, being itself a heat insulator. The usual insulating material is fibrous material in the form of sheets, but treated paper in the form of micanite and Bakelite cylinders and sheets are used. The insulation must not deteriorate up to temperatures of 95° C. or under the influence of oil, and must not show any acid tendency.⁵

Enamelled Films.—To remove the difficulty of the hygroscopic properties of cotton, the wires may be covered directly with an elastic enamel and be used without further protection. The wire is drawn through the varnish and dried rapidly by being passed through a stove heated to 275°-280° C. and the temperature is carefully controlled. The stoving heat is much above the point of carbonisation of cotton, and owing to the relatively small thickness of the enamelled film the dimensions of the coils may be considerably reduced (see table below). The varnish consists of a pitch-resin-linseed-oil mixing with suitable thinners, and the coating must be elastic. Some enamelled films are on a soluble cellulose basis and do not require the high stoving of the enamels containing pitches.

Copper Wire.	Diameter in Mms.	
	1.	2.
Bare	0.12	0.5
Enamelled	0.14	0.52
+ 1 layer cotton	0.17	0.57
+ 2 layers „	0.22	0.6
+ 1 layer silk	0.145	0.525

The requirements are the production of a uniform layer which is unchanged by sun or moisture, and unflammability when placed 20 mm. above a burning flame. The films must stand bending around a rod four times the diameter of the wire without cracking, and after heating at 150° C. for ten hours they must show the same elasticity. They must be able to withstand an elongation of 10 per cent without cracking.

The breakdown voltage for wires of $\frac{1}{2}$ mm. or 1 mm. diameter must be 500 volts or 250 volts, according as the electric tension is

applied between two layers of wire or between one layer of wire and the metal cylinder around which it is wound. A third method of testing is by running the wire continuously through a mercury bath and applying electric tension between the mercury and the wire. A voltage of 60 is sufficient for the test. The wire is passed through the mercury bath at the rate of 15 metres per minute, and not more than 400 ruptures per kilometre or one rupture every $2\frac{1}{2}$ metres should occur. Enamelled wires are used in

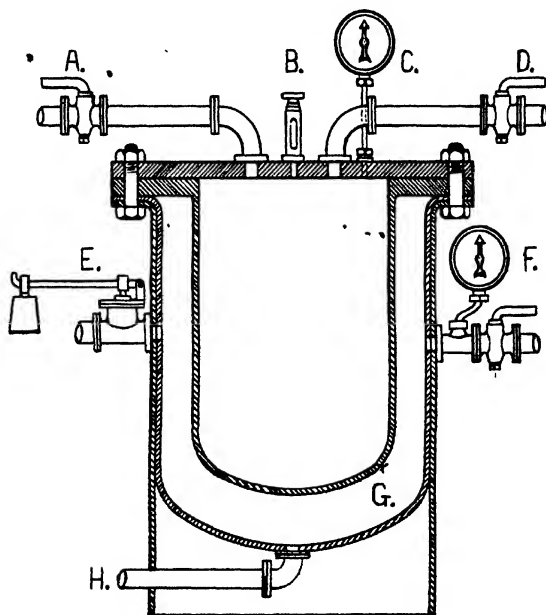


FIG. 43.—Bakeliser.

A = Compression tap.
B = Safety valve.
C = Pressure gauge.
D = Exhaust tap.

E = Safety valve.
F = Steam gauge.
G = Steam chamber.
H = Steam valve.

interruptor coils, telephone receivers, electric bells, induction coils, and transformer coils.

Bakelite Varnishes.—Reference has been made in an earlier chapter to the uses of Bakelite for insulating purposes. Its heat-dispersive power is said to be slightly superior to oil or pitch insulators, so that accidents due to overcharge and overheating are avoided. Paper impregnated with Bakelite is used in the manufacture of Micarta sheets, Pertinax tubes, and transformer terminals. The process is to impregnate with the varnish, and, after drying, a sufficient number of sheets of paper are pressed together or rolled

into tubes; in this way cylinders 3 ft. in diameter and transformer terminals from 6 to 9 ft. long are produced which will stand 100,000 volts.⁷ The dielectric strength of Bakelite is 53,700 volts for $\frac{1}{16}$ in., or 20,000 volts per mm., compared with 50,400 volts for $\frac{1}{16}$ in. shellac paper. The Bakelite paper has good mechanical resistance and elasticity, so that it can be bent on itself and made easily into tubes.

Bakelite A requires a stoving heat of 140°-170° C. under ordinary pressure. If the materials after impregnation be heated in a jacketed Bakeliser under a pressure of 150-250 lb. per sq. in., the change into Bakelite B can be brought about in five to ten minutes (Fig. 43).

Resinite of Lebach can be stoved hard at 80°-90° C. to give complete hardness. The liquid Bakelite serves for impregnation for dynamo work and penetrates satisfactorily into the windings, giving a solid block on stoving. It is not hygroscopic.

Bakelite C is not suitable for impregnation, being inelastic. It is generally incorporated with asbestos, etc., and on heating becomes insoluble and infusible.

Bakelite has not as yet replaced impregnating compounds, in spite of its high dielectric properties and its power to resist acids, chlorine, and weak alkalis. It is stated that the difficulty of dismantling of parts insulated with Bakelite is considerable.

It may be asked, "Is it advisable to re-varnish or to re-impregnate after a period of use?" The best materials will deteriorate in time. Re-impregnation will mean dismantling of the parts of the machine, a course which is advantageous, but entails putting the machine out of action for a considerable time. In the majority of cases re-impregnation is not necessary, and it is sufficient to clean the surface from dust and oil and to apply a coat of air-drying varnish by means of a brush or by dipping.

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CHAPTER XVII

DRYING OIL AND OIL-VARNISH ANALYSIS

Drying Oils

IN the examination of a drying oil it is advisable to determine (1) specific gravity, (2) iodine value, (3) acid value, (4) saponification value, (5) amount of unsaponifiable matter, (6) the moisture content, (7) the percentage of oxidised acids, (8) the refractive index, (9) the ether-insoluble bromide value of the oil or its corresponding acid, (10) the drying time of the oil against a standard linseed oil, (11) the amount of mucilage, (12) the colour, and (13) the viscosity. Nos. 1, 2, 3, 4, 9, 10, and 11 are generally essential. In the case of China wood oil the determination of the refractive index is of importance.

I. SPECIFIC GRAVITY

The methods employed require either a specific gravity bottle or a Sprengel tube, but generally the Westphal balance is preferred, especially when considerable quantities of the oil under examination are available and it is not too viscous. For works practice an ordinary hydrometer is the most convenient. For directions as to the use of all these instruments reference may be made to Fryer and Weston, *Oils, Fats, and Waxes*, vol. ii. With the exception of China wood oil (s.g. 0.940 (15.5° C.)) all the drying oils have specific gravities lying between 0.925 and 0.933.

II. IODINE VALUE

This is a valuable guide as to the drying power of an oil, and represents the percentage of iodine absorbed by an oil from a suitable reagent. Hübl found that iodine in alcoholic solution in the presence of mercuric chloride was quantitatively absorbed by unsaturated fats and oils. The Hübl method requires the following solutions: (a) iodine solution, which is prepared by dissolving 25 grams of iodine in 500 c.c. of 95 per cent alcohol and mixed with 30 grams of mercuric chloride dissolved in 500 c.c. of 95 per cent alcohol. These solutions should be mixed only when required and the mixture be allowed to stand twenty-four hours

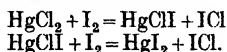
before use; (b) a standard solution of sodium thiosulphate; (c) a solution of potassium iodide, free from iodate. The solvents for the oils are chloroform and carbon tetrachloride, and they should be pure. Ether may not be used, but benzol (free from thiophene) or glacial acetic acid may be employed.

The determination of the iodine value is carried out as follows: From 0.15 to 0.18 gram drying oil (0.2-0.3 gram semi-drying oil) is weighed off accurately into a bottle of 500-800 c.c. capacity, provided with a well-ground stopper. The oil is dissolved in 10 c.c. chloroform or carbon tetrachloride, and 25 c.c. iodine solution run in from a pipette. In order to prevent loss of iodine by volatilisation it is advisable to moisten the stopper with potassium iodide solution. The solvent and the iodine solution must give a clear mixture, otherwise more solvent must be added. The mixture must exhibit a dark brown colour after twelve to eighteen hours in the case of drying oils, otherwise 25 c.c. more of the iodine solution must be added to maintain excess of iodine; 15-20 c.c. of potassium iodide are added, the mixture is well shaken and diluted with 400 c.c. water. If a red precipitate of mercuric iodide appears, more potassium iodide must be added. Standard thiosulphate is run in until both water and solvent layers are only slightly coloured; starch solution is added, and the titration finished in the usual manner. Immediately before or after the titration with thiosulphate, 25 c.c. of the original iodine mercuric chloride solution are treated in the same manner so as to form a blank experiment. The difference between the amounts of iodine found, calculated in terms of iodine to units per cent of the sample, will give the iodine value. When the titrated solution has stood for some time it becomes blue again, due to reversal of the reaction with the splitting-off of iodine, but this does not interfere with the accuracy of the titration. The values obtained by Hübl's method are quite concordant, provided an excess of iodine, not less than the amount actually absorbed, has been employed and the operations are performed under identical conditions. It is necessary that two atoms of iodine for one molecule of mercuric chloride be present.

It must be pointed out that the position of the double bond in the unsaturated oil fat or acid influences the iodine absorption; thus, oleic acid shows an iodine value 89 (calc. 90), whereas maleic shows an iodine value nil (calc. 219). If the double bond be distant from the carboxyl group, as in oleic acid, the iodine value is normal, whereas if it be adjacent to the carboxyl group the iodine value is lower than the calculated figure.

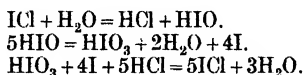
Waller has proposed a modification of the Hübl solution on the following lines: 25 grams iodine in 200 c.c. strong alcohol and 25 grams mercuric chloride in the same amount of solvent are mixed with 25 grams conc. hydrochloric acid (s.g. 1.19) and made up to 500 c.c. with alcohol. Rather less mercuric chloride is used than in the original Hübl solution, and Waller's solution is, moreover, twice as concentrated as the original Hübl. Although the results obtained by the use of Waller's solution are in general agreement with those

of Hübl when oils and fats are tested, yet in the case of mineral oils, cholesterol, and naphthenic acids, the results are at variance with those obtained by the previous method. The scheme of the Hübl reaction may be expressed as follows :



The reaction, which is incomplete and reversible, may be best expressed by the two equations given above.

In the presence of water the following reactions may occur simultaneously :



Of the reaction products HIO and HIO₃ will react in the presence of hydrochloric acid to give iodine.

The addition of hydrochloric acid in the Waller's solution inhibits the first reaction and prevents hypiodous acid being formed, which would oxidise the alcohol and so disturb the equilibrium. If absolute alcohol be used the solution becomes more stable. Ingle² considers that the formation of free hydrochloric acid in the reaction is due to the decomposition of the iodine chloride addition product, and the amount of free hydrochloric acid formed depends on the chemical structure of the unsaturated compounds.

Wijs' Modification of the Hübl Process.—Wijs' iodine solution³ may be prepared in two ways :

(a) 7.5 grs. iodine trichloride and 8.2 grs. of resublimed iodine are dissolved separately in recrystallised glacial acetic acid on the water bath, taking care that the solution does not take up moisture. The two solutions are then poured into a litre flask, which is then filled up to the mark with glacial acetic acid. A more convenient way is to dissolve a 10 gram tube of iodine trichloride in 300 c.c. glacial acetic acid and add a 2½ per cent solution of iodine in the same solvent until the iodine is slightly in excess. The mixture is then made up to one litre with freshly recrystallised glacial acetic acid.

(b) Dissolve 13 grs. iodine in a litre of *good* glacial acetic acid, withdrawing 100 c.c. for later use, and pass dry chlorine into the iodine solution until the brown colour changes to a clear orange tint. The iodine solution, held in reserve, is now added until the colour of the solution becomes faintly brown. The slight excess of iodine prevents the formation of iodine trichloride. The solution is stabilised by heating on the water bath for about twenty minutes and kept in the dark in a well-stoppered bottle. The solution maintains its strength for several months, if pure materials have been employed. The glacial acetic acid used must be freshly frozen out and should give no green tinge on heating with potassium bichromate and concentrated sulphuric acid, showing freedom from formic acid.

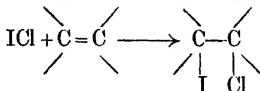
The Wijs solution is allowed to react with a drying oil in the same manner as the Hübl, but for a much shorter time; half an hour to six hours may be required according to the degree of unsaturation of the glyceride. If acetic acid reacts with the oil, the Hübl solution must be used.

Details of the Method.—0.15 gr. of a drying oil is dissolved in 10 c.c. of purified chloroform or carbon tetrachloride and 25 c.c. of the Wijs solution added, taking care to moisten the stopper of the bottle containing the mixture with potassium iodide solution, and allowed to stand for one hour. In the case of oils having a high iodine value, like linseed, it is advisable to allow the mixture to stand for 2-3 hours. The stopper and neck of the bottle are washed down with 15 c.c. of a 10 per cent potassium iodide solution and 100 c.c. of distilled water added, and the excess of iodine titrated with the standard sodium thiosulphate solution. Towards the end of the titration about 2 c.c. of the starch solution are added, and the contents of the bottle are shaken vigorously after each addition of the thiosulphate solution, until the contents of the bottle are colourless.

A blank test, using 10 c.c. of the oil solvent and 25 c.c. of the iodine solution, must be done with each set of estimations. The result is expressed as a per cent of iodine reacting with the oil.

The Hånus solution⁴ contains iodine bromide instead of iodine chloride and is considered by American chemists to be superior to the Wijs solution, and its use is recommended in American standard specifications of linseed oil.⁵

The principle of the Wijs or Hånus method is simple :



Sundberg and Lundborg⁶ state that the Hånus method gives results with fats which agree closely with those found by the Hübl method; Wijs' method gives higher results. In the case of linolic acid the Hübl value lies nearer to the theoretical than does the Wijs value. Marshall⁷ proposes carbon tetrachloride as solvent, and Aschmann prepares a solution of iodine chloride with water, by passing chlorine into potassium iodide solution until the iodine liberated is redissolved, and after filtering from potassium iodate the solution is allowed to react with a chloroform solution of the oil or fat for twenty-four hours. The values lie between those obtained with the Wijs and Hübl solutions.⁸

Kelber and Rheinheimer⁹ prefer Wijs' method, because of the greater stability of the solution and the rapidity of the process. MacLean and Thomas¹⁰ have investigated the behaviour of sterols (cf. cholesterol) with Hübl and Wijs' reagents; with sterols the Hübl solution gave values approximating to those required by the number of double bonds believed to exist in the sterol molecule. With the Wijs reagent the results may be twice as high as those

obtained with the Hübl solution, and vary greatly with the temperature, time of contact, and proportion of the reacting substances. The difference in behaviour of the two reagents appears when they react with the sterols (not with reduced sterols), with the resinic acids, and possibly with the naphthenic acids, though in the latter case, definitely, substances of known constitution have not been investigated. The effect appears to be due to the influence of the glacial acetic acid used in the solution as solvent for the iodine chloride, and affords evidence that a considerable amount of substitution takes place. The substitution effect is particularly noticeable when a condensed ring-nucleus containing one double bond reacts with Wijs' solution; thus abietic acid, containing two double bonds, and dihydroabietic acid, containing one double bond, give identical values with Wijs' solution, so that substitution must be much greater in the reduced derivative. Anthracene reacts similarly with Hübl and Wijs' solutions, giving high iodine values in both cases, but phenanthrene and retene (isopropylmethyl phenanthrene) are hardly affected by Hübl's solution, and absorb considerable amounts of iodine from Wijs' reagent.

Compounds of iodine with unsaturated compounds have been isolated; e.g. trichlorotriiodostearic acid, $(C_{18}H_{30}O_2I_3Cl_3)$ (m.p. $146^\circ C.$) obtained by the action of iodine monochloride on a linolenic acid and tribromotriiodostearic acid, $(C_{18}H_{30}O_2I_3Br_3)$ (m.p. $124-126^\circ C.$) (p. 14). By shaking with lime water the calcium salt $(C_{18}H_{30}O_2I_3Br_3)_2Ca$ is obtained. For drying oils, the Wijs method may be recommended as most convenient, but in dealing with ring compounds the Hübl method is perhaps safer, owing to the tendency for substitution to occur when Wijs' solution is used.

III. ACID VALUE ✓

The acid value may be expressed as the number of milligrams of potash required to neutralise the free fatty acids in one gram of oil. It is also stated in the terms of percentage of free oleic acid in the oil, this acid being selected as a typical fatty acid occurring in vegetable oils.

To determine the acid value of an oil, 5 grams are weighed and 50 c.c. of alcohol or methylated spirit (previously neutralised) are added and the mixture gently boiled. The solution is cooled, 1 c.c. phenolphthalein added, and then titrated with $N/10$ or $N/2$ alkali. The acidity may be expressed in milligrams of potash per gram of oil, or in percentage of oleic acid:

$$\text{Acidity} = \frac{a \times N/10 \text{ alkali} \times 2.82}{\text{Weight of oil taken}} \quad \begin{matrix} \cdot 2.82 & \text{M.W. of oleic acid.} \\ a = & \text{No. c.c. of standard alkali.} \end{matrix}$$

At the end of the titration not less than 50 per cent of alcohol ought to be present in the mixture.

The acid value is a variable, depending on the quality of the sample and on the mode of extraction of the oil from the seed.

Rancidity will increase the acid value, and oxidation brings about the same result. A few acidity standards are taken from the Report of the Committee of Analysts on the standard methods of analysis of seeds, nuts and kernels, fats and oils, and fatty residues (Ministry of Food, Oils and Fats Branch):¹¹

		Percentage of Oleic Acid.
Linseed oil	{ Raw	2
	{ Refined	2
Soya oil	{ Crude	2.5
	{ Edible	0.15
Cotton seed oil	{ Crude, Indian	2.5
	{ Egyptian	4
	{ Technical refined	0.3
	{ Fine edible	0.15

IV. SAPONIFICATION VALUE

The saponification or Köttstorfer value represents the amount of potassium hydroxide required to neutralise the free and combined acid constituents of a fat or oil, and is expressed in terms of parts of potassium hydroxide per 1000 parts of the fat or oil.

Solutions required: (a) N/2 hydrochloric acid, accurately standardised. Sulphuric acid is not advisable, because potassium sulphate may be precipitated in the titration of an alcoholic solution and interferes with the end reaction; (b) an alcoholic solution of potassium hydroxide, approximately N/2, prepared by dissolving 18.20 grams of stick potassium hydroxide in not more than 10 c.c. of distilled water, and mixing up to 500 c.c. with 94-95 per cent (by volume) alcohol. The solution is allowed to stand for twenty-four hours, and the clear liquid siphoned off for use. The alcohol must be free from mineral oil and of such a purity as to yield a colourless solution of alkali after twenty-four hours. If methylated spirit be used, it should be purified by the method proposed by Waller.¹²

The Test.—About 2 grams of the clear oil are accurately weighed into a 200 c.c. flask of resistance glass, 25 c.c. of neutral alcohol added, and 25 c.c. of the alcoholic potassium hydroxide solution, accurately measured, run in. A like quantity of the same solution is run into a similar flask, together with 25 c.c. of the neutral alcohol. The flasks are connected to reflux condensers or long air condensers and heated on a boiling water bath for half an hour. The flask containing the oil should be shaken with a rotary movement from time to time during the period. The contents of the flasks are then titrated while hot, with the N/2 acid, after the addition of 1 c.c. of a 1 per cent alcoholic solution of phenolphthalein. A = grams of oil taken. B = c.c. of acid required in the control experiment. C = c.c. of acid required to neutralise the excess of alkali in the test.

$$\text{Saponification value} = \frac{(B - C) \times 0.2805 \times 1000}{A}$$

If the solution be dark it may be diluted with strong alcohol, and alkali blue used as an indicator. The saponification values of a few principal drying oils are as follows :

Linseed oil, 192.5 ; China wood oil, 193 ; Perilla, 189.6 ; Soya oil, 193 ; Para rubber seed oil, 206 ; Poppy seed oil, 195.

The saponification value, as determined by the above method, includes the alkali required for the neutralisation of any free acid in the oil, and the acidity must be subtracted from the saponification value to give the true saponification value.

The acid value and saponification value may, if so desired, be determined upon the same weight of the sample in the following manner :

About 4 grams of the clear oil are accurately weighed into the saponification flask and 25 c.c. of hot alcohol, containing 1 c.c. of phenolphthalein solution and previously neutralised, are added. The free fatty acids are titrated from a burette with the alcoholic alkali solution, as used for the saponification value, warming if necessary during the titration. The number of c.c. required by the free fatty acids having been noted, such a further quantity as will make a total of 50 c.c. is added and the process continued as described above.

A blank test is made with 50 c.c. of the alcoholic alkali delivered from the identical burette, using similar quantities of all the reagents. The exact value of the alcoholic alkali having been determined with N/2 hydrochloric acid, the acid value and saponification value may be respectively calculated.

V. UNSAPONIFIABLE MATTER

Unsaponifiable matter in fats and oils includes all substances which are insoluble in water, but soluble in the fat solvents specified below, after alkali saponification of the fats and oils. It is taken to include alcohols (other than glycerine) ; *e.g.* sitosterol (phytosterol) in the case of vegetable oils, and cholesterol in the case of animal oils and fats. (Certain fish oils contain unsaponifiable hydrocarbons (squalene, etc.). Some waxes yield insoluble alcohols on treatment with alkalis. The unsaponifiable matter generally remains dissolved in the soap solution after saponification. The principle of the method of estimation depends on the solubility of the unsaponifiable matter in ether or in petroleum ether, whereas the soaps are practically insoluble, whether they are in solution or in the dry state. It is better to use ether than petroleum ether, and to get rid of any soap, which may have been taken up into the ether by wax alcohols or hydrocarbons, by treatment with a little water and re-extraction with ether.

The method recommended by the Committee of Analysts (*loc. cit.*) is as follows : Saponify 5 grams of the oil with 50 c.c. of approximately normal alcoholic potassium hydroxide, boiling under a reflux condenser for sixty minutes with occasional shaking. Transfer the alcoholic solution to a separating funnel ; rinse the

flask successively with 50 c.c. of methylated ether, 50 c.c. of petroleum ether, and 50 c.c. of water. Transfer the rinsings to the separating funnel, shaking well after each addition. Allow to separate and withdraw the soap solution. Repeat the extraction of the soap solution twice, using ether and petroleum ether as before, omitting the treatment with water. The combined ethereal extracts are washed by shaking with slightly alkaline water, allowing to settle, and running through a filter into a tared flask. Wash the filter with petroleum ether, distil off the solvent, dry at 100° C., and weigh the unsaponifiable matter. Any fatty acids present in the extracted matter are determined volumetrically as oleic acid and their amount deducted from the weight.

The amount of unsaponifiable matter in natural oils and fats is very variable, but in genuine samples it is quite small; *e.g.* linseed oil, raw or refined, contains 1 per cent of unsaponifiable matter. Soya oil (crude or edible) contains also 1 per cent.

Determination of Oil in Seeds, Nuts, and Kernels.—It may be advisable to indicate here a standard method for the estimation of a drying oil present in oil seeds, nuts, and kernels. The method recommended is as follows:¹¹

Extract a weighed quantity of the sample prepared for analysis with petroleum ether (volatile without residue at or below 60° C.) in a suitable apparatus for two hours. Remove the partially extracted material, dry, grind in a mortar (grinding may be facilitated by the addition of 1 gram of fine sand), and again extract until exhausted. If the sample contains a large percentage of oil, it is advisable to grind twice, extracting after each grinding. Evaporate off the solvent, dry at 100° C., and weigh. In the case of oils liable to rapid oxidation, like linseed, drying should be conducted in an inert atmosphere. The extracted oil must be free from solid matter and completely soluble in petroleum ether. .

VI. MOISTURE

The amount of moisture contained in an oil is variable, depending on its age and period of tanking. A good linseed oil should not contain more than 0.25 per cent of moisture. The connection between moisture and mucilage content will be referred to later. The method recommended may be described as follows:¹¹

A U-tube, one limb of which is an ordinary narrow-bore glass tube and the other a tube of 1½ in. in diameter, is charged in its wider limb with soft blue Cape asbestos, which has been dried at 100° C. The wide limb is provided with a rubber stopper through which passes a narrow tube bent at right angles. The tube, without the stopper, is accurately weighed, suspended by a wire, and about 20 grams of the well-mixed sample of oil or fat are dropped on to the asbestos, and the whole re-weighed. The stopper is then inserted, and the tube which passes through the stopper is connected with a Kipp apparatus supplying hydrogen, thoroughly dried by passage through strong sulphuric acid. A U-tube, such as is used

in elementary analysis and provided with two glass taps, is filled with glass beads which are afterwards moistened with strong sulphuric acid. This tube is accurately weighed, after having been previously filled with dry hydrogen, and is then connected with the narrow limb of the asbestos-charged tube, the latter being suspended in a beaker containing water kept at a temperature about 10° C. above the melting point of the fat under examination. A slow current of hydrogen is now passed through the whole. When no trace of condensed moisture can be seen in the horizontal limbs of the oil tube and of the weighing tube, which is generally the case after one hour, the latter is weighed, then again attached, and a current of hydrogen allowed to pass for another hour. Minute traces of volatile organic matters, as a rule, produce slight darkening of the sulphuric acid. The asbestos may be advantageously used in the form of a very porous felt paper, produced by pulping the asbestos and running the pulp into a centrifugal, which is lined with linen.

As an alternative method capable of dealing with a number of samples in one operation, stoppered weighing bottles of about the dimensions of the wider limb of the U-tube used in the standard method may be charged with asbestos, or alternatively with strips of pleated blotting paper or with paper pulp. These tubes are dried in a vacuum desiccator containing sulphuric acid and kept at a pressure of 2.5 mm. After weighing, about 2 grams of the fat or oil are placed in each tube, which is again weighed. The tubes are warmed until the fat under examination is melted, and then replaced in the vacuum desiccator. The air is exhausted and the desiccator is kept in an incubator at 20° C. for at least forty-eight hours. The weight after that time remains practically constant.

This standard method is applicable, in the opinion of the Analysts' Committee, to all fats and oils, whether readily oxidisable, like linseed oil, or containing high percentages of free fatty acid of low molecular weight, such as lauric. In the case of fats and oils which are free from uncombined fatty acid and not readily oxidisable, the ordinary methods of drying on sand in a water oven may often be used, provided the results are in agreement with those furnished by the standard method. In the writer's opinion it is doubtful whether all the moisture is removed by the above method if the oil under examination contains much mucilage.

VII. OXIDISED FATTY ACIDS

Some drying oils on exposure to air become viscous, owing to the formation of oxidised glycerides, and blown oils contain the same substances, whose formation is accompanied by a reduction in the iodine value of the original oil. Fahrion estimates the amount of oxidised acids in the following manner: 4.5 grams of the sample are saponified with alcoholic potash; the alcohol is evaporated off, the soap is dissolved in hot water, transferred to a separating funnel, and decomposed with hydrochloric acid. After

cooling, the liquid is shaken with petroleum ether (b.p. below $80^{\circ}\text{C}.$) and allowed to stand until it has completely separated into two layers. The insoluble oxidised fatty acids will be found to adhere to the sides of the funnel or form a sediment in the petroleum ether layer. The aqueous layer is drawn off and the petroleum ether removed, if necessary, through a filter, and the oxidised acids are washed with more petroleum ether to remove adhering fatty acids. If the amount of oxidised fatty acids be large, it is advisable to dissolve them in alkali, decompose the resulting soap with hydrochloric acid, and shake out again with petroleum ether to remove any soluble fatty acid. The oxidised acids are then dissolved in warm alcohol or ether, the solution evaporated in a tared dish, and the residue weighed. Linseed oil blown for ten hours at $120^{\circ}\text{C}.$ will contain 7.1 per cent oxidised acids. Linseed oil blown with oxygen until its I.V. = 58.8 contains 42.82 per cent oxidised acids.

VIII. REFRACTIVE INDICES OF OILS AND VARNISH THINNERS

The ease with which the refractive index can be determined makes the refractometer of importance in the examination of vegetable oils and of varnish thinners. The refractive index does not give a perfectly reliable means of detecting adulteration, but it serves to indicate generally whether a sample is genuine or not. For the use of the refractometer in the analysis of oils and fats reference must be made to a paper by J. N. Goldsmith.¹³ The optical principles underlying the refractometers now in use and their employment in chemical analysis have been given by Philip,¹⁴ and it is unnecessary to describe here their construction or manipulation.¹⁵ The Abbé and Pulfrich forms are the most popular, and for the determination of dispersion the Pulfrich instrument is the more suitable.

The application of the refractometer for controlling the identity or quality of oils is well known. It is of value in testing the contents of a large number of packages when it is impossible to make a complete analysis of each sample.

Weger¹⁶ has measured the refractive indices of a large number of treated linseed oils:

Indian linseed oil at $25^{\circ}\text{C}.$	1.4728
Cold "boiled oil" with 1 per cent PbMn resinate at $25^{\circ}\text{C}.$	1.4736
" " " 2 " " " "	1.4743
" " " 3 " " " "	1.4748
" " " 5 " " " "	1.4760
The same, heated one hour at $150^{\circ}\text{C}.$	1.4766
Cold "boiled oil" with 1 per cent Mn linolate at $25^{\circ}\text{C}.$	1.4733
The same heated two hours at $150^{\circ}\text{C}.$	1.4740
Boiled Indian linseed oil, 0.5 per cent PbO, 0.2 per cent MnO,	
two hours at $230^{\circ}\text{C}.$	1.4759
Indian linseed oil, clarified at $280^{\circ}\text{C}.$	1.4739
" " " heated 40 hours at $180^{\circ}\text{C}.$ - $190^{\circ}\text{C}.$	1.4789
" " " 5 min. at $360^{\circ}\text{C}.$	1.4842
" " " blown 20 hours at $150^{\circ}\text{C}.$	1.4854
" " " 25 " " "	1.4868

The small differences in the figures for boiled oil show that refractometric determination is of no avail in differentiating between various samples, but when the oil has been thickened the refractive index rises.

Morrell¹⁷ determined the refractive radius of polymerised linseed and China wood oils :

Linseed oil, thickened at 260°-280° C. in CO ₂ (s.g. 0.969) n_D 19° C. .	1.4915
Acetone soluble portion (s.g. 0.9527) n_D 19° C. .	1.4864
Acetone insoluble portion (s.g. 0.9763) n_D 19° C. .	1.4964
Tung oil (s.g. 0.9405) n_D 14° C. .	1.5172
Thickened tung oil (s.g. 0.956) n_D 15° C. .	1.5134

Schapringer¹⁸ also noted the remarkable fact that when China wood oil is heated the refractive index falls with the iodine value although its specific gravity increases; that this is not due to oxidation is shown by the fall in the refractive index when the heating is performed in an atmosphere of nitrogen¹⁹ (cf. Wolff).

The following table shows the effect on boiled oil of storage for eighteen months under different conditions. The figures in brackets under the refractive indices are "Oxygen Absorption" determined by weighing films.

	In Darkness. Open.	In Darkness: Air-tight	In Light: Open.	In Light: Air-tight.
Cold boiled oil with 3 per cent PbMn resinate	1.4877 (10.9)	1.4807 (17.2)	1.4873 (13.4)	1.4804 (17.6)
Oil heated with 3 per cent PbMn resinate	1.4881	1.4812	1.4893 (11.8)	1.4812 (16.2)

- China wood oil has a high refractive index, and adulteration with other oils can be detected by the lowering of the value of the refractive index. The difference between the figures for tung oil and Soya oil at 40° C. being 0.0402, the addition of 10 per cent or even 5 per cent Soya oil could be detected. The Refractometry Committee of the Society of Chemical Industry recommended readings to be taken at 20° C. for oils. The mean temperature correction per degree centigrade is 0.00036.^{19a} Instead of measuring the refractive indices of oil it is sometimes preferable to determine the refractive indices of the corresponding acids.

Refractive indices of the mixed fatty acids of linseed oil and China wood oil at 20° C. :²⁰

100 per cent linseed oil fatty acids . . .	1.4666
95 " " " " . . .	1.4707
90 " " " " . . .	1.4775
80 " " " " . . .	1.4824
50 " " " " . . .	1.4895

In the examination of varnish thinners the refractometer is of use in analysing a large number of binary solvent mixtures. The percentage of white spirit present in a mixture of turpentine

and white spirit can be determined with fair accuracy from the value of the refractive index, for the relationship is expressed by a linear graph. Similarly a mixture of benzol and petrol or a mixture of benzol and turpentine can be estimated from the value of the refractive index of the special mixture. It must be pointed out that the presence of benzol in a mixture of white spirit and turpentine would invalidate the method, as it only holds for binary mixtures.

Optical Dispersion.—Little attention has been paid to dispersion measurements. Fryer and Weston²¹ have measured the dispersion of a number of oils and have found that for tung and coconut oils the dispersions are unusually high and low respectively. The difference between the refractive indices of any two rays of the spectrum of a refractive medium is termed the dispersion of that medium. The dispersive power (ω) of a substance is expressed by the ratio of the coefficient of dispersion to the index of refraction of the mean ray, less unity. If n_c , n_D , and n_F represent the refractive indices of a substance for the C, D, and F lines of the spectrum, then the dispersion of the substance is $n_c - n_F$ for the F and C lines, and its dispersive power (ω) = $\frac{n_c - n_F}{n_D - 1}$.

The dispersive power of tung oil is 0.371, linseed oil 0.0218, menhaden 0.0207, and coconut 0.0167. The values are of much less analytical importance than the refractive indices. The drying and semi-drying oils are broadly differentiated from the non-drying oils and fats, but the separation is not very marked. Oxidation of an oil increases the dispersion, while heating (polymerisation) produces a marked decrease, and this may afford a means of distinguishing oxidised from polymerised oils.* With varnish solvents aromatic hydrocarbons (benzol, toluol, xylol) have dispersive power from 0.033-0.031, whilst petroleum, naphtha, and turpentine have the values from 0.0208 to 0.0209.

Holley²² uses a method which does not depend on numerical measurements, but on the inversion of spectrum colours shown by tung oil when examined in the Pulfrich refractometer. An addition of not less than 15 per cent of pure linseed oil to tung oil under examination should restore the normal position of the colored bands. If less than 15 per cent is required the oil is considered to be adulterated, while very pure oils have required an addition of as much as 22 per cent. In general, the refractive index increases uniformly with decreasing wave length, except in the neighbourhood of an absorption band. The absorption band may lie in the ultra-violet region, as in the case of carbon disulphide, which has a strong dispersion. The dispersive power is connected with the molecular structure; e.g. benzol has a higher dispersive power than tetrahydrobenzol and also than hexylene; naphthalene than benzol; and quinoline than naphthalene. For mixtures of fatty oils and fatty acids the refractive index will give more rapid

* "Elaidins" give much lower dispersions than the oils from which they are produced.

results, but the measurement of the dispersion will serve to corroborate the opinion already formed on the nature of the oils or acids under examination.

HEXABROMIDE TEST FOR LINSEED OIL AND OTHER OILS. HEXABROMIDE NUMBER

The unsaturated oils or acids, when treated under proper conditions with bromine, absorb two atoms of the halogen at each unsaturated linkage. The solubility in ether of the bromo-derivatives decreases with increased bromine content, so that the octo- and hexabromides are only very sparingly soluble, whereas the tetra- and di-bromo bodies are soluble. The fatty acids are generally used, because the glyceryl esters give non-concordant results. Many investigators have examined the condition under which bromine is absorbed by unsaturated oils and acids. Hehner and Mitchell²³ have investigated the combination with glycerides. Eibner²⁴ and Muggenthaler²⁵ have investigated the compounds formed with fatty acids. The details of Eibner's method are as follows: 2 grams of mixed fatty acids prepared from the oil under examination are dissolved in sufficient dry ether to give a 10 per cent solution and cooled to -10° C. 0.5 c.c. bromine is delivered very slowly (twenty minutes) from a fine-drawn pipette into the ethereal solution. The remainder of the bromine (0.5 c.c.) is added slowly, so that the total time of bromination is half an hour. The temperature must not rise above -5° C. during the bromination. The flask containing the mixture is allowed to stand for two hours at -10° C. The ethereal solution is carefully decanted on to a weighed filter paper and carefully washed with five lots, each of 5 c.c., of cooled ether. After complete draining the precipitate is dried for two hours at 80° - 85° C. and cooled in a desiccator. The melting point of the hexabromide obtained in this manner from linseed oil acids is 177° C. and not 182° C., which may result when the precipitate has been dried at a higher temperature. The octobromides are also insoluble in ether, but are sparingly soluble in benzol, in which the hexabromides are very soluble. The octobromides do not melt below 200° C. It is generally advisable to determine the percentage of bromine in the insoluble precipitate to decide on the presence of the octobromide.

Bailey and Baldisiefen²⁶ state that they have examined the published methods for the hexabromide value of linseed oil and found that the results obtained are not concordant. They recommend the following method:

(a) *Preparation of Fatty Acids*.—Weigh approximately 50 grams of oil into a 2-litre round-bottom flask and add 40 c.c. of caustic soda solution (s.g. 1.4) and 40 c.c. of alcohol. Place the mixture on a steam bath and heat for about half an hour, passing a stream of carbon dioxide through the apparatus all the while. Add one litre of hot distilled water and boil the soap solution, either over a free flame or on a steam bath, to remove the alcohol.

After removing the alcohol the solution is cooled somewhat and then acidified with dilute hydrochloric acid (1:1). Warm the mixture until the fatty acids form a clear layer, continuing to pass carbon dioxide through the system. The fatty acids are separated in a separating funnel from the aqueous layer and washed thoroughly with hot distilled water until the washings are neutral to methyl orange. The warm fatty acids are freed from water by centrifuging and kept in a well-stoppered bottle.

(b) *Preparation of the Hexabromides.*—Weigh accurately 1 gram of fatty acids into a weighed centrifuge tube (1 in. diameter and 5 in. long). Dissolve the fatty acids in 25 c.c. of specially prepared ether. The ether is washed with 10 per cent of its volume of ice-cold distilled water. After separating the water and repeating the washing three times, the washed ether is dried over fused calcium chloride and the drying completed by means of sodium. After distillation the ether is treated with an excess of finely powdered hexabromide of the fatty acids of linseed oil previously prepared. Decant the ether solution, kept at least for three hours at zero, into a dry bottle.

To the fatty acids dissolved in ether a bromine solution (5 c.c. bromine and 25 c.c. glacial acetic acid made up just before use) is added very slowly until a deep red colour is produced. The tube is then allowed to stand in an ice-chest over night (about fourteen hours). The solution is separated from the precipitate by centrifuging and the precipitate repeatedly washed with the specially prepared ether and the last traces of the ether removed in a vacuum. The precipitate is then weighed.

In the Steele and Washburn method²⁷ the fatty acids are dissolved in 10 c.c. of dry chloroform containing 3 per cent by volume of absolute alcohol. The solution is cooled to $-5^{\circ}\text{C}.$, and a bromine solution (bromine 1 volume, chloroform 2 volumes) is added slowly from a burette until an excess is present. The excess of bromine is removed by the addition of a few drops of amylene. The chloroform is removed at $50^{\circ}\text{--}60^{\circ}\text{C}.$ under reduced pressure. After removal of the chloroform the precipitate is washed with ether prepared according to the previous method. After four ether washings the precipitate in the tube is freed from ether by heating in a bath at $60^{\circ}\text{--}70^{\circ}\text{C}.$ for fifteen minutes in a vacuum. The total weight of the precipitate $\times 100$, divided by the weight of the fatty acids taken, gives the hexabromide percentage.

It is considered that Steele and Washburn's method has not been displaced by Bailey's modification, although the latter points out that if ether be used in the bromination it is not necessary to prepare a special chloroform solution and the slight excess of bromine does not affect the final result, so that the use of amylene is unnecessary. It is essential that an ether saturated with linseed oil hexabromides be employed, as they have a slight solubility in ether, which is appreciable even at $0^{\circ}\text{C}.$

Eibner²⁸ considers that Bailey's method gives lower values than the methods of Eibner and Steele, and he states that fish oils

can be detected by the benzol test or by separation of the clupanodonic acid as lithium salt. Tschudy²⁹ points out that the experimental error of Bailey's method may produce results differing by ± 6 per cent from the actual amount of linseed oil in the mixture, but generally in mixtures of linseed and soya bean oil the modified hexabromide method gives more nearly accurate results than those obtained by the iodine number determination.

The following table shows the percentages of insoluble bromides obtained from drying oils or their acids:

	From Glycerides.	From the Acids.
Perilla oil	53 per cent	64.0 per cent. (Eibner).
Linseed oil, I.V. 181	23.1-23.5 *	42.0-50.0 (Steele and Pailey).
" " I.V. 204	49.3	
" " I.V. 190.4	37.72	
" " I.V. 180	35.2	
Tung oil	0	0
Menhaden oil	61.8	51.5 (Gemmell).
Cod liver oil	42.9	35 (Gemmell). ³⁰
Soya bean oil	3.73	4.2-6.5 (Steele and Bailey)

* Walter and Warburton (m.p. 140° C., decomposes at 155° C.).

	Percentage of Bromine.
Dibromostearin	35.19
Tetrabromostearin	53.23
Hexabromostearin	62.28
Octobromostearin	68.92

The properties of the bromine addition products of unsaturated fatty acids are:—

- Oleic acid (Dibromo), 36 per cent bromine.
- Linolic acid (Tetrabromo), m.p. 113°-114° C., 53.3 per cent bromine—sparingly soluble in petroleum ether.
- Linolenic (Hexabromo), m.p. 180°-181° C., 63.32 per cent bromine—very slightly soluble in alcohol, cold ether, glacial acetic acid, and in cold CCl₄, soluble in hot CCl₄, almost insoluble in petroleum ether.
- Clupanodonic, C₂₂H₃₄O₂ (Decabromo), blackens at 200° C. and decomposes above that temperature, 69.87—very slightly soluble in most organic solvents; e.g. alcohol, ether, CCl₄, glacial acetic acid, petrol, and CCl₄.
- Arachidonic acid C₁₉H₃₁CO.OH (Octobromo), blackens at 220° C. and decomposes above that temperature. Insoluble in all organic solvents.

X. COMPARISON OF THE DRYING TIME OF AN OIL AGAINST A STANDARD LINSEED OIL

Two methods may be employed, the first depending on the gain in weight on oxidation in the presence of driers, and the second on the time of drying and the condition of the surface of a film of the oil which has been treated with driers. The second method is preferable, as it is directly practical. In reference to the first method, Livache determined the gain in weight when 1 gram precipitated lead is treated with 0.5 grams of a drying oil.

Oil.	Gain in Weight per cent in		
	One Day.	Three Days.	Five Days.
Bombay linseed . . .	2.18	8.11	9.67
" " . . .	1.16	4.81	5.14
Plate . . .	1.16	4.64	5.14

The Committee E on Preservative Coatings (1900) U.S.A.³⁰ concluded that the results obtained by using litharge as a drier in place of lead were not generally satisfactory. Liverseege and Elsdon^{30a} modified the method examined by the above-mentioned committee and obtained more satisfactory results. Ten grams litharge (40 sieve) were spread in a thin layer on a flat dish and kept at 20° C. over night. 0.7-0.9 gram of drying oil were added, followed by 5 c.c. methylated ether, so as to give complete mixing with the litharge, and the gain in weight on oxidation was determined after two days' exposure. Genuine raw linseed oil ceases to gain weight after two days, and the gain in weight is 15-18 per cent. Genuine boiled linseed oil ceases to gain weight after one day, and the total gain in weight is 12-14 per cent. Whilst drying oils do not gain weight after two days, non-drying oils may continue to gain weight for weeks. When oils of a particular class are compared, the gain in weight varies with the iodine value and there is evidence of some relationship between the figures in oils of different classes.

Oil.	Gain in Weight per cent in		
	One Day.	Two Days.	Three Days.
Linseed	17.4	16.9
Boiled linseed . . .	14.1	13.6	..
Soya	8.4-8.9	..
Cotton seed	6.6	..
Whale	6.4	..
Rosin	9.9 and 19.4 in 13 days	

The second type of method is to prepare a drying oil containing known amounts of lead and manganese driers. A similar linseed drying oil is prepared and the drying times of the two films on glass or wood are compared. In a recent War Office specification (C.W.D./404, 1920) for raw linseed oil nine volumes of the oil are mixed with one volume of a 25 per cent solution of precipitated manganese resinate in turpentine (C.W.D./408), and the mixture is exposed in the form of a thin film on glass, in a vertical position at a temperature of 15.5° C. The film must dry in a manner not

inferior to that of a film of the approved tender sample, when tested at the same time and under identical conditions. Attention must be paid to the quality and appearance of the film, because some drying oils—*e.g.* perilla—give peculiar surfaces with irregular markings.

XI. MUCILAGE

Mention has been made in a previous chapter of the mucilage content of drying oils. The amount present in a sample of oil may be determined in the following manner: 15 c.c. of the oil are placed in a test tube ($\frac{3}{8}$ in. \times 6 in.) and heated over an open flame to 300° C., the temperature being determined by a thermometer suspended in the oil. The rise in temperature should not exceed 50 degrees per minute. A linseed oil containing mucilage "breaks" at 260° C. and flakes of the mucilage appear. The oil is then cooled down to the ordinary temperature and at once centrifuged in a graduated tube. A good linseed oil shows 2-3 per cent mucilage by volume. If the oil be allowed to stand over night after breaking, "the foots" are too finely divided to be removed by centrifuging. The American Society for Testing Materials state the breaking tests for linseed oil, but make no recommendation as to their estimation.³⁰ The writer has found the above method convenient and satisfactory.

XII. COLOUR

The colour of linseed oil can be standardised by a Lovibond's tintometer.

XIII. VISCOSITY

The viscosity of a drying oil may be determined by any of the methods described under the Viscosity of Varnishes.

Linseed Oil.	Tung Oil.	Olive Oil.	*Water.
212 secs. (Redwood).	858-1433 secs.	312 secs.	25.4 secs. (Redwood) at 70° F.

Separation of Saturated Components of Drying Oils from Unsaturated Components.—The lead salts of saturated fatty acids are insoluble in ether, whilst those of the unsaturated acids are soluble. The examination of a drying oil for its content of saturated fats, stearin, palmitin, etc., is described by Lewkowitsch.³¹

The quantitative separation of the lead salts of the saturated acids from those less saturated by means of ether was examined by Varrentrap (1840) and Renaud.³² If the fats contain the glyceride of linolenic acid it is stated that it is impossible to obtain the saturated fatty acids in an approximately pure state by fractional precipitation of the lead salts in three solvents—alcohol, chloroform, and ether—although the method works well in mixtures of saturated and less unsaturated acids.

The separation of the unsaturated acids by means of their oxidation products produced by potassium permanganate, viz. hydroxystearic acids, has been investigated by Hazura, and the

details are given in Lewkowitsch's *Oils, Fats, and Waxes*, 5th ed., vol. i. 574. A. Grün³³ points out that linolic acid may give four tetrahydroxystearic acids $C_{18}H_{36}O_6$, and linolenic acid may furnish 32 hexahydroxystearic acids $C_{18}H_{36}O_8$.

Linseed Oil Substitutes.—When the price of linseed oil is high, adulterants appear. If the sample under examination has an abnormal drying time, specific gravity, iodine value, and saponification value, adulterants may be suspected. The possible impurities are rosin oil, mineral oils; *e.g.* benzine, kerosene, or lubricating oil, fish oils, soya bean oil, corn oil, and hemp or rape oils. China wood oil is unlikely, because of its high cost. The cheapest and commonest adulterants are the mineral oils, which are lighter in weight than linseed oil and reduce its specific gravity as well as saponification value. Rosin oil is frequently added to compensate for this reduction. Fish oils are often used for general outside work, specially on the sea coast, and for application to hot surfaces, as in the preparation of smoke-stack paints. It is advantageous to use a mixture of menhaden oil with linseed up to a proportion as high as 75 per cent of the mixture. The oils have a disagreeable smell and cause darkening of linseed oil. The presence of fish oils can be detected by the ether-insoluble-bromide test.

The most objectionable linseed oil substitutes are those consisting of solutions of rosin and hydrocarbon oils, with which are mixed tar-oil and rosin. Such vehicles possess little permanence. The rosin would be indicated by the high acid value of the oil and the Liebermann-Storch reaction. Rosin oil is commonly employed as a substitute, but it remains sticky and dries very slowly, and, if used as a paint, it will damage any subsequent coat. Corn oil is sometimes used as a substitute in Canada, but as it is a semi-drying oil its use to any considerable extent will delay the hardening of the film. Soya oil is regarded as a partial substitute for linseed oil, and its presence in linseed oil will reduce both the iodine value and the drying time. Other substitutes may be obtained by dissolving metallic resins in tar oil and petroleum. In the examination of the ignited residue for metals—*e.g.* lead and manganese—or of the aqueous solution after saponification, treatment with dilute nitric acid and extraction of organic material with ether are followed by the usual methods. Hemp and rape oil are rarely used as adulterants, owing to their higher cost. There is at present no oil on the market at a reasonable price which can entirely replace linseed oil with complete satisfaction to the user. For general purposes the addition of any of the above, with the exception of tung oil, will diminish the value of linseed oil. Raw soya oil as a substitute for linseed oil is preferably first blown, then given a heat treatment to thicken it, and a drier of manganese, lead, and cobalt, liquefies in the proportions of 0.03 per cent, 0.2 per cent, and 0.01 per cent respectively is added. Such an oil is considered by some to be a fair substitute for linseed oil. Lumbang oil, mixed with linseed oil has not proved satisfactory, although it is probably more durable on exposure than linseed oil alone.

The Adulterants of China Wood Oil.—Owing to the increasing demand for tung oil the detection of adulterants is of importance. The commonest are soya, perilla, and lumbang (*Aleurites moluccana*) oils. The detection of the adulterants is based on (1) differences in optical dispersion; (2) polymerisation or gelation tests.

Reference has already been made to the importance of the refractive index of China wood oil. Ware³⁴ has shown that tung oil will give a dispersion of 269 units in his special apparatus, whilst soya bean oil shows only 129 units.

The detection of tung oil in varnish mixings depends on the same two factors, *i.e.* the high refractive index of the oil [1.5179 (20° C.)]; linseed oil 1.4835 (15° C.)] or its corresponding acid, and the easy gelation of the oil or acid. The polymerisation test has been studied by Gardner,³⁵ who has put forward a test devised by Browne.

Browne's Test for Purity of China Wood Oil.—The test tubes containing the oil should be 16 × 15 mm. with a mark near the bottom to indicate 5 c.c., and closed by a cork so perforated that a glass rod 3 mm. in diameter can move freely. Fill a copper beaker (height 12 cm.; internal diameter 6 cm.) with cotton seed oil to a height of 7.5 cm. Place a thermometer so as to be 1.5 cm. from the bottom of the bath. Use a nitrogen-filled thermometer with an engraved stem; total length 4-4½ in., graduated from 210°-310° C. in two intervals, the length between 210° and 310° C. being not less than 2½ in. If preferred, use an emergent-stem thermometer 30 cm. long with graduations from 100°-400° C., making corrections for the emergent stem according to the method outlined in the stem correction sheet, N. 44, U.S. Bureau of Standards. When the temperature of the bath is 293° C. (560° F.) and very slightly rising at this point, place the tube, containing 5 c.c. of the oil to be tested, so that the bottom is level with the lowest part of the bulb of thermometer. Note the time, remove the source of heat for about forty-five seconds, and then reapply. Before two minutes have elapsed the temperature of the bath will have fallen to 282° C. (540° F.), at which point it should be kept as steady as possible. When the tung oil has been in the bath almost nine minutes, raise the glass rod at intervals of half a minute, and when the rod is firmly set note the time. A sample of good tung oil should gelatinise in twelve minutes. As the setting or gelation takes place within a few seconds of fluidity, a good end-determination is afforded. Remove the specimen at once, heat the bath again to 293° C., and repeat the experiment with another portion of the sample. No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached. When the cotton seed oil has become heavy and viscid it should be removed, otherwise the heating may be irregular.³⁵

Jameson³⁶ has shown that the time required to polymerise tung oil by heat increases with the fatty acid content, and in the Browne's test the presence of 1.9-4.5 per cent free acid extends the time by 1.2-5 minutes. If the oil be mixed with dry slaked lime it will,

if genuine, polymerise within twelve minutes when heated to 282°C . It is possible to detect the presence of 5-10 per cent of adulterating oil by means of the gelation test. The addition of perilla oil alone would raise the iodine value, whereas soy^a would depress it, but both would reduce the refractive index and retard the gelation of the oil. The addition of lumbang oil will likewise retard the solidification of the oil on heating and reduce the refractive index. The writer attaches more practical value to the heat test than to the determination of the refractive index.

OIL-VARNISH ANALYSIS

The characteristics of a good varnish have been dealt with in a previous section. The status of varnish analysis is not good, and in the opinion of Pearce³⁷ it is doubtful whether it gives any idea of the comparative practical values of any two samples of varnishes, because it is so difficult to identify the component resins and the state of the oil present in the mixing. The determinations which are usually made comprise thinners, resins, oil, and driers. For controlling the products in the factory the tests include specific gravity, viscosity, flash point, colour comparison, drying tests on glass or on a prepared wooden panel, and the examination of the hardness of the film and of its rubbing properties, as well as the action of hot and cold water. It is evident that the above tests give inadequate information as to the durability of the coating, which can only be determined satisfactorily after six or nine months' exposure. An attempt has been made to connect the elasticity, ash-content and the water absorptive power with the durability (see p. 284). It has been suggested that the behaviour of the film towards 20 volumes hydrogen peroxide is a valuable guide to the resistance of the film to oxidation. The dependence of the properties of a varnish film upon the composition of the varnish, as indicated by the analytical results, is by no means certain, owing to the difficulty in estimating the proportions of resin to thick oil and the want of connection between the properties of the separated resins and the physical and chemical constants of the sweated gums. The separation and estimation of the thinners is comparatively simple and fairly accurate.³⁸ The changes which occur in the ageing process modify the properties of the component resins and oil. Pearce (*loc. cit.*) has examined the methods put forward by Boughton, Darner, Twitchell, and Scott, and finds that of the first named to be the best.

The great difficulty in varnish analysis is the separation of the resin acids from the oil and the identification of them when separated. The esterification which is involved in the methods put forward by the investigators, whose names have been mentioned above, is based on the fact that in the presence of an esterifying agent fatty acids and ethyl alcohol react to form esters, while rosin acids either do not or do so very incompletely. In the Twitchell method³⁹ dry hydrochloric acid gas is passed into a solution of the mixed resin

and oil acids in absolute alcohol. The details of Wolff's method of esterification⁴⁰ are as follows: Between 2 and 5 grams of the mixed resin and fatty acids obtained after saponification of the varnish freed from thinners, are dissolved in 10-20 c.c. absolute methyl or ethyl alcohol and esterified by boiling for two minutes under a reflux condenser with 5-10 c.c. of a solution of one part of sulphuric acid in four parts of ethyl or methyl alcohol. The esterified mixture is treated with five to ten times its volume of a 7-10 per cent solution of common salt, in which any oxy-abietic acid is insoluble, and the fatty acid esters and free resin acids are extracted with ether or a mixture of ether and petroleum ether. The salt solution is drawn off and re-extracted once or twice with fresh solvent. The extracts are then washed with salt solution until the washings have a neutral reaction. After the addition of alcohol, the ethereal solution is titrated with N/2 alcoholic potash, and in the case of mixtures of rosins and oils the percentage of rosin acids is calculated on the assumption that they have an acid value of 160. The percentage thus found is reduced by 1.5 to allow for the fatty acids which escape esterification.

After neutralisation of the rosin acids 1.2 c.c. excess of alcoholic potash may be added, the ethereal solution washed several times with water, the mixed washings and soap solution evaporated to a small bulk, acidified, and after addition of an equal bulk of salt solution, extracted with ether. The ethereal solution is dried over anhydrous sodium sulphate and ether evaporated. The residue is dissolved in 10 c.c. absolute alcohol, re-esterified, and extracted in the manner already described. The rosin acids thus obtained are free from fatty acids which have escaped esterification in the first treatment. The amount of rosin present in the mixture is obtained by multiplying the percentage of rosin acids by 1.07 per cent, to allow for 7 per cent of unsaponifiable matter in the rosin. When this method is used for the analysis of varnishes which contain resins yielding material insoluble in petroleum ether, the insoluble matter must be separated. If appreciable amounts of resins (other than rosin) remain dissolved in the petroleum ether, the volumetric method cannot be used, since the viscous resins have different neutralisation values.

Pearce's⁴¹ modification of Boughton's method is as follows: From 4-6 grams of varnish are weighed into 125-c.c. Erlenmeyer flask, 25 c.c. of water added, and the mixture boiled over a very small flame until only a few c.c. of water remain. After the removal of the volatile thinners 25 c.c. each of 0.5 N. alcoholic potash and benzene are added and the mixture refluxed for one hour. The solution is evaporated to about 10 c.c. and transferred to a 500-c.c. separating funnel, washing the flask with alcohol, water, and ether. The use of ice-cold ether and ice-cold water is recommended, and very small quantities of alcohol are added when required to break up the emulsion. Water and ether, 100 c.c. of each, are added, and the mixture well shaken. The shaking is repeated three times. The ether layer is washed well with water and separated. A weighed

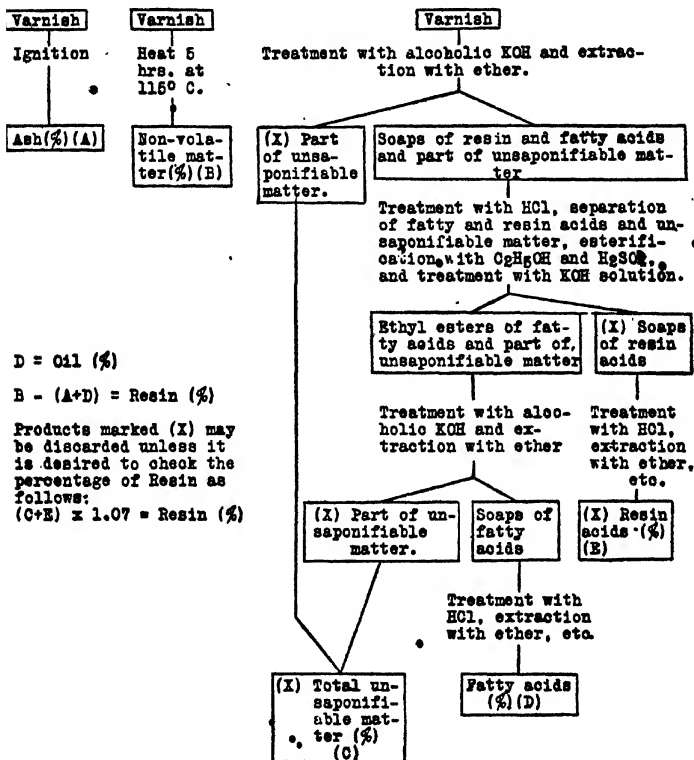
Erlenmeyer flask, labelled "Gums," is used to receive the ether layer from the separating funnel. The flask containing the first part of resins (C_1) separated from the other constituents is set aside and only used to receive the ether extracts of resins or unsaponifiable matter (C and E).

The aqueous layer and washings are acidified with hydrochloric acid, completely extracted with ether, and the ether separated from the fatty and resin acids and the remainder of unsaponifiable matter by distillation. To the flask are added 20 c.c. of absolute alcohol and 20 c.c. of a mixture of 4 parts of absolute alcohol with 1 part of concentrated sulphuric acid, and the contents heated with reflux condenser for five minutes. The mixture is shaken in a separating funnel with 100 c.c. of ether and 100 c.c. of a 10 per cent solution of sodium chloride. The ether layer is separated and washed with water and the aqueous layer and the washings of the ether layer are extracted with 50 c.c. of ether. The combined ether extracts (the aqueous layer is discarded) are treated with 50 c.c. of 0.2 N. aqueous potassium hydroxide and 10 c.c. of alcohol, and well shaken after the layers have separated at least twice. The ether layer is treated with 50 c.c. of water containing 5 c.c. of 0.2 N. potassium hydroxide and 5 c.c. of alcohol, and after settling the aqueous layer is combined with the original one. These layers are extracted completely with ether and all the ether layers combined and washed. The aqueous portion is acidified with hydrochloric acid, the resin acids (E) extracted with ether, transferred to the flask labelled "Gums," and the solvent distilled off. The ether layers are transferred to the flask and the solvent removed as before. The residue is refluxed with 25 c.c. of 0.5 N. alcoholic potash for one hour and the last of the unsaponifiable matter (C_2) removed by two or more extractions with 50-c.c. portions of ether. The extracts are added to the "Gums" flask, the solvent removed, the contents (C + E) dried on a steam bath overnight and heated to constant weight in a drying oven at 110° - 120° C. The aqueous layer is acidified as before, completely extracted with ether, and the ether layers washed with water. The ether layer is transferred to the flask and the solvent removed. The flask and contents are heated on a steam bath overnight, or until all the water is removed, and then heated in the oven to constant weight (D).

The diagram on the following page illustrates the method used.

Determination of Rosin.—*Qualitative (Liebermann-Storch Reaction).*—Rosin may be detected qualitatively as follows: 5 c.c. of the varnish are poured into a small separating funnel with 5 c.c. of carbon disulphide, the mixture shaken, and 10 c.c. of acetic anhydride added. After complete separation into layers, 1 or 2 c.c. of the lower acetic anhydride layer are poured into an inverted crucible cover, and 1 drop of sulphuric acid (34.7 of sulphuric acid to 35.6 of water) is carefully added by means of a stirring-rod to the edge of the cover, so as to mix slowly with the acetic anhydride, when a characteristic fugitive violet colour results, if rosin be present. Wolff⁴⁰ suggests the following modification of the

Liebermann-Storch method, which is more general for all forms of rosin likely to occur in a varnish. Five grams oil-varnish are dissolved in 150 c.c. ether, and the solution shaken twice with 250 c.c. of a 1 per cent solution of either ammonium carbonate or caustic soda. The water extract, after acidification with hydrochloric acid, is extracted with ether. The ether solution is evaporated, the residue dissolved in ten times its bulk of petroleum ether, and 3 or



4 drops of this solution are used for the Storch reaction. The addition of ammonia to the rest of the petroleum-ether solution will cause gelatinisation if rosin be present.

Quantitative.—The rosin may be estimated following the directions given under Wolff's method previously described, and in view of increasing quantities of rosin in varnishes nowadays the question becomes of considerable importance. W. T. Pearce⁴² has examined M'Ilheney's method for analysis of oil varnishes, which

includes the estimation of rosin. The sample is saponified with an excess of caustic potash dissolved in absolute alcohol, and enough glacial acetic acid dissolved in absolute alcohol is added to liberate the fatty and resin acids. Then petroleum ether is added, thoroughly mixed, and the strong alcoholic solution is diluted with water, thus causing the petroleum ether to separate. This ether layer is supposed to contain only the rosin and fatty acids, the "hard gums" being insoluble in this solvent. After the solvent is distilled off, the residue is dissolved in absolute alcohol and esterified by Twitchell's method to separate fatty acids from the rosin. Using this method, Boughton found that the petroleum ether solution would contain resin acids in cases where no rosin was present. Pearce concludes that the above method, or any method based on the difference of solubility of the resin acids in petroleum ether, is inapplicable. From a theoretical standpoint this is precisely what would be expected. Rosin is a resin containing unsaturated acids not unlike the resin acids contained in Zanzibar, kauri, manila, and Congo gums. The free acids in rosin are largely neutralised before the material is made into varnish. During the running of the gums 15-30 per cent loss occurs, and in the heating changes in acidity are often observed.

The following results are given of the saponification, acid, and ester values of rosin and kauri separated from an oil varnish:

Varnish.	S V.	Acid V.	Ester Value.
Straight rosin varnish .	182-185	160-162	22-24
1/2 rosin, 1/2 kauri ..	122-135	44-62	72-78
1/2 " 1/2 " ..	143	88	55
Kauri varnish .	130	45	85
Untreated kauri .	124	41	83
" rosin .	165-180	155-170	13

6. The identification of the gums separated from the oil is uncertain. The determination of the acidity and iodine value may furnish indications as to the presence of a hard or soft copal resin in the varnish. A high percentage of unsaponifiable matter indicates the presence of dammar.

The Examination of the Fatty Acids separated from the Resins.—

Part of the acids obtained from the resin-oil separation may be used to study the properties of the oils used in the manufacture of the varnish. The estimation of tung oil may be carried out according to the method given by Pearce³⁷ and the hexabromide test may be used for the detection of menhaden oil.

Wolf⁴³ saponifies the non-volatile part, removes the resin acids, and determines the index of refraction of the fatty acids. The presence of wood oil will be indicated by a value higher than that given by linseed oil. The presence of tung oil will also be indicated by the gelation of the fatty acids obtained; e.g. a mixture of tung

oil, menhaden oil, and linseed oil in the proportion of 1 : 1 : 2 gave fatty acids, which gelatinised on heating, whereas a mixture containing linseed, soya, and cotton oils gave no coagulation.

De Waele⁴⁴ describes a method which Wolff⁴⁵ considers to be the best published. The method is somewhat involved in manipulative details, and the reader is referred to the original paper. The volatile thinner is estimated by a simplified method of distillation with water.⁴⁶ The non-volatile residue is saponified with strong potassium hydroxide in benzol-alcohol, the soap evaporated to dryness, taken up with water, acidified under ether, and the aqueous layer, consisting of the mineral matter present as drier, separated off and discarded. The acid ethereal layer is then shaken up with excess of potash and the unsaponifiable matter remaining in the ethereal layer estimated in the usual way. Much unsaponifiable matter indicates the presence of dammar, which is insoluble in acetic anhydride. The intermediate step of acidification of the soap solution, with subsequent reconversion into soap, has for its object the removal of lead, calcium, etc., which might be present from rosinsates and which would subsequently interfere in the separation of the resins from the oils. The soap freed from unsaponifiable matter is then acidified under petroleum ether (b.p. 35°-60° C.), whereby "gum-resin acids" separate as a flocculent intermediate layer. These are removed, dissolved in ether, and weighed. The petroleum-ether layer containing the resin acids from rosin and gum resin, together with fatty acids from the oil, is then evaporated to dryness and esterified by Wolff's or Twitchell's method. An equal volume of petroleum ether is added, the acid present neutralised with normal alkali, and water added to an amount sufficient to dilute the alcohol to 60 per cent strength. This ensures adequate separation of the alcohol and petroleum-ether layers, whilst inhibiting hydrolysis of the rosin soap. The aqueous layer is then separated, the petroleum ether layer re-extracted with water several times, and the extracts united. The aqueous extract is finally acidified under ether, which latter will then contain the resin acids from rosin and part of the gum resin. The gum acids previously referred to may be tested for fossil gum acids, oxy-fatty acids, and oxyabietic acid:

	For H Gum Acids.	Oxy-fatty Acids.	Oxyabietic Acid.
70 per cent acetone, cold	Insol. or nearly so, not liquefied	Quite sol.	Softened to a liquid.
Boil with saturated borax solution	Insol. or nearly so	Quite sol.	Quite sol.
Alcoholic KOH	Nearly insol.	Easily sol.	Easily sol.
N/2 NaOH in absolute alcohol	Insol.	Insol.	Quite sol.

• The percentage of oil is obtained by difference. If gum resin and rosin are present, the resin acids will be made up of these

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accruing from the true rosin and those from the gum resin; the latter, however, usually contributes a proportion of resin acids represented by 10 per cent of the "gum acids" found. When rosin is introduced in a varnish with gum resin, it has not suffered any prolonged or excessive heat treatment, so that its original composition is maintained.

ROSIN

Unsaponifiable matter	about 10 per cent.
Oxyabietic acid (petrol-ether insol.)	2.5 "
Rosin acids	85 "

In calculating his results de Waele treats the two following cases separately:

(a) Gum Resin and Rosin present.

- (i.) True rosin acid due to rosin = per cent rosin acids - $\frac{\text{"gum acids"}}{10}$ per cent.
- (ii.) Unsaponifiable matter due to rosin = $\frac{(i.)}{10}$
- (iii.) Oxyabietic acid in rosin = neglect.
- (iv.) True gum-resin acids = "gum acids."
- (v.) Unsaponifiable matter due to gum resin = total unsap. - (1 per cent + ii.).
1 per cent is deducted as being due to oil.

$$\text{Gum resin per cent} = \frac{(iv.) + (v.)}{0.7}; \text{rosin per cent} = (i.) + (ii.)$$

(b) Gum Resin and Rosinate Drier (including "hardened" Rosin) present.

In consequence of the heat treatment in the preparation of the rosinate, and of the destructive distillation to neutral hydrocarbons and oxidation which the resin acids in rosin undergo, the organic matter in rosinate averages out as follows:

Unsaponifiable matter	20 per cent.
Oxyabietic acid	20 "
Rosin acids	60 "

The calculation of the results is very similar to that in the preceding case.

- (i.) True rosin acids due to rosin as in case (a).
 - (ii.) Unsaponifiable matter due to rosin = $\frac{(i.)}{5}$
 - (iii.) Oxyabietic acid in rosin = (ii.).
 - (iv.) True gum-resin acids = "gum acids" - (iii.).
 - (v.) Unsaponifiable matter due to gum resin as in previous case.
- $$\text{Per cent gum resin} = \frac{(iv.) + (v.)}{0.7} \text{ and per cent rosin} = (i.) + (ii.) + (iii.)$$

Oxy-fatty acids ("oxidised acids" of Fahrion) do not coexist with resins in varnishes to any appreciable degree. They exist in many enamel media varnishes containing no gum resin, where oxy-fatty acids may be found in fair quantities. An attempt to estimate

rosin in such litho-oils has been made on the assumption that "oxidised acids" are the products of saponification. Thus, on acidifying the varnish, oxidised oil will not be affected, whilst partly neutralised rosin (rosinates) will confer on the varnish the acidity originally due to the rosin acid present; e.g. 2.3 grams of the varnish are dissolved in excess of ether or ether-benzol, and the solution shaken up with 2 successive lots of dilute hydrochloric acid. The acid layer is run off and the ether layer washed with water or dilute sodium chloride solution until the washings are quite neutral. Alcohol is added and the solution titrated with deci-normal potassium hydroxide. The calculation of the rosin present in rosinate by means of the determination of the ash is valueless, as the basicity of these products varies considerably.⁴⁴

It is evident that the separation of resin and oil is not yet satisfactory, although it has been much improved. The identification of China wood oil is now more certain, but the estimation of its amount is not yet reliable. The quantity of polymerised linseed oil in a varnish is difficult to determine with certainty. An attempt has been made in treating the varnish with acetone after the removal of thinners and treating the soluble and insoluble portions separately for resin and oil content.⁴⁷ The results show the presence of more polymerised oil than was expected, but they are explicable on the assumption that polymerisation had taken place during the manufacture and ageing of the varnish. Further investigation in this direction is desirable. Using Twitchell's method with varnishes of known composition and made in bulk, the results obtained by the writer of the resin, oil, and thinners estimation compared with the calculated values will give a rough idea of the degree of accuracy of the method used, provided the esterification has not been carried so far as to produce appreciable quantities of esters of the resin acids.

	1.		2.		3.		4.	
	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.
Turps .	41.8	41.6	41.4	45.3	40.5	43.5
Oil .	43.3	41.8	38.7	38.2	38.8	38.8	42.3	40.3
Resin .	13.1	15.3	16.3	17.4	13.8	14.0	14.8	14.9
					3.0	1.9	6.8	1.3 Dryers
	98.2	98.7			97.0	100.0	98.4	100.0

The writer is of the opinion that etherification by hydrochloric acid at a low temperature until saturation is more reliable than Wolff's method. Excessive etherification gives too high a percentage of oil, and *vice versa*. The examination of the resins and oils separated in analyses 3. and 4. shows the differences between the original and separated oils and resins.

	Original Oils.	Separated Oils (Ethyl Esters).	Original Resins Sweated.	Separated Resins.
Iodine value	170	92-106	109	83-85
Saponification value . .	190	172	130	101-110
Acid value	1-2	1-4	28	27

Guesses may be made as to the nature of the resin, but so much depends on the conditions of sweating that resins only of extreme types can be differentiated; *e.g.* rosin and congo, or congo and manila. In the chapter on Resins it has been pointed out how difficult it is to identify the mixture of resins from the values of the so-called constants. A large amount of unsaponifiable resin is indicative of dammar (dammar is partly saponifiable, and the unsaponifiable portion is partially soluble in petroleum-ether). *Smitt-Addens*⁴⁸ states that in the case of dammar resin a portion is easily saponifiable, whilst another is unsaponifiable, the latter being partly soluble in petroleum ether, whilst the former is soluble in ether only. Should dammar be suspected, the soap is further extracted with ether and the extract evaporated, when a light-colour residue indicates its presence; extraction with chloroform or carbon tetrachloride will serve to separate copal.

*Fortini*⁴⁹ puts forward a method for the estimation of resins in soaps by treatment with nitric acid, which gives nitro-derivatives of resins insoluble in petroleum ether. The method is also applicable to soaps containing resins other than colophony.

Acid Values of Varnishes.—The acidity of a varnish is of importance, especially if it is to be used with pigments. The acid values of varnishes (linseed oil or spirit varnishes) can be determined by boiling with alcohol and titrating with standard alkali solution, in the presence of phenolphthalein. If the varnish contains oils which have been bodied by heat or by blowing, the acidity cannot be satisfactorily determined by the ordinary methods. It is advisable to replace the alcohol by a mixture of equal volume of previously neutralised benzol and alcohol. In the presence of benzol it is much easier to obtain a sharp neutralisation point.⁵⁰

The acidities will vary essentially with the resin content, so that short-oil varnishes are more acid than long-oil varieties. The writer prefers to state the acidity on the gum-oil content by estimating separately the percentage of thinners; *e.g.*:

	Acidity.	Acidity calc. on Gum-oil Content.	Percentage of Thinners.
Flattening	20.8	31.5	33.9
Polish	29.6	57.3	48.6

Ordinarily the linseed long-oil copal varnishes will have acidities varying between 14 and 20. Where neutralisation with glycerine and lime has occurred the acidity may fall to 8 or 12 (calculated on gum-oil content). It must be pointed out that a certain acidity of the resin tends to preserve the brightness of the varnish mixings.

Analysis of Bituminous Varnishes.—In Boughton's scheme of varnish analysis the asphaltic pitches would be found in the primary unsaponifiable matter, together with part of the stearine pitch material. The saponifiable part of the stearine pitches would be found in the fatty oils and acids, whereas the resin pitches would appear in the resin acids portion. It is evident that the presence of copals and rosin will make the interpretation of the results very difficult; nevertheless, it is possible to form a fair opinion as to the amounts of the components, if the examination proceeds according to the following scheme (Abraham, p. 571).

Examination of Pigment and Filler in a Bituminous Varnish.—Dilute 100 grams of the well-mixed material with 500 c.c. benzol in a 800 c.c. stoppered flask. Allow to stand in a warm place until the pigment or filler has settled, then carefully decant the supernatant liquid into a clean flask of large capacity. The pigment or filler is shaken up with 250 c.c. more benzol and allowed to stand in a warm place until it settles, and the supernatant liquid is decanted into the second flask. Repeat the treatment with benzol until the vehicle has been completely extracted from the pigment, decant through a weighed Gooch crucible provided with an asbestos filter. The residues in the flask and in the Gooch crucible are washed with benzol as before and combined with the balance of the pigment or filler, which is dried at 110° C. and weighed. The pigment or filler will contain any free carbon black or coal-tar pitch carbon. The benzol extracts are evaporated at 110° C. to exactly the calculated weight of the base, by subtracting the weight of the solvent and the pigment or filler from the original solution of material taken for examination, preferably in an atmosphere of coal gas. The base is then examined as follows: Dissolve 50 grams in 150 grams of benzol, add 10 c.c. dilute nitric acid (1:1), and boil under reflux for half an hour to decompose metallic soaps (driers). Add 150 c.c. water, and boil again under reflux to remove the nitrates of the metallic driers. Repeat the extraction with hot water, and separate the benzol solution of oils, pitches, and resins. The benzol solution is distilled to 100 c.c. bulk, and

boiled under reflux with 300 c.c. of a 10 per cent alcoholic potash solution (100 grams caustic potash, 500 c.c. 95 per cent alcohol, and diluted with 90 per cent benzol, to a litre) for one hour, and the unsaponifiable material separated. It is advisable to examine the unsaponifiable material for cholesterol or phytosterol by the Liebermann-Storch reaction, and, if they be present, to heat 2 grams of the unsaponifiable material with 4 c.c. acetic anhydride under reflux for one hour. After addition of 25 c.c. of ethyl alcohol (95 per cent) and heating to boiling, the liquid is decanted through an asbestos Gooch crucible filter and the residue washed with warm alcohol to remove acetic anhydride. The residue is then dried at 100° C. and weighed, as representing the hydrocarbons (pitches and unsaponifiable resins). The filtrate from the acetic anhydride treatment is evaporated to dryness and dissolved in the smallest quantity of hot absolute alcohol and allowed to cool. The acetates of the alcohols crystallise out. They are filtered off and the crystals washed with 95 per cent alcohol and dried. Cholesterol acetate melts at 114° C., whilst phytosterol acetate melts at 120° C. If after 5 or 7 recrystallisations the melting point is below 115°-116° C., phytosterol may be considered to be absent. The above higher alcohols are mixed with the unsaponifiable constituents of the resins, which amount to 4-8 per cent of the resins present. The examination of the hydrocarbons may be carried out as given in Chapter X. and under Boughton's scheme (p. 337). The saponifiable matter is dealt with under the same scheme or by others previously mentioned. The difficulties of distinguishing between the fatty acids derived from the vegetable oils and those from the fatty pitches which may be present are very great. The following differences may be considered as a guide only :

	Fatty Acids from Oils.	Fatty Acids from Pitches.
Lactone value	Less than 25	Greater than 25.
K. and S. fusion point .	" " 80 C.	" " 80.
Hardness at 77 F. . . .	" " 5	" " 5.
Colour in mass	Translucent yellow to brown	Opaque brown to black.

It is evident that in a mixture of oils and pitches it is impossible to obtain a quantitative result of the two kinds of fatty acids.

Detection and Estimation of Metallic Driers in Varnishes.—The chief metals to be detected are lead, manganese, cobalt, and calcium. Small quantities of zinc and iron are often found in varnishes, in addition to magnesium and phosphates, which are components of oil mucilage. Generally the examination is restricted to the detection of lead, manganese, cobalt, and calcium.⁵¹ The ordinary tests and methods of estimation may be performed on the ash obtained on incineration of the varnish. Nevertheless, for qualitative purposes, there is great saving of time if the varnish

can be treated directly by reagents which will detect the metals referred to above.

• *Lead.*—The detection of lead is simple. The varnish may be incinerated and the ash examined by the usual methods, viz. extraction with hot nitric acid followed by filtration and addition of sodium acetate solution and potassium bichromate. A yellow precipitate of lead chromate indicates the presence of lead, which may be confirmed by addition of a solution of ammonium sulphide, whereby the lead chromate would be transformed into black lead sulphide.

Incineration of the varnish is not necessary, because by using hot dilute nitric acid the lead can be extracted from the varnish and the solution tested as above. A more rapid method is to dilute with an equal quantity of light petroleum in a test tube and shake well the varnish for two minutes with a dilute solution of potassium bichromate. If lead be present there is no sharp line of division between the two liquids, owing to a precipitate of lead chromate at the dividing surface and also on the walls of the test tube. If the contents of the tube be carefully poured away the lead chromate is found to stick to the glass, and its presence can be confirmed by treatment with ammonium sulphide. The test works in the presence of manganese and cobalt.

Manganese.—The presence of manganese or cobalt can be detected without incineration of the varnish by the following method: The varnish is diluted with an equal volume of light petroleum, a little water and a few drops of potassium hydroxide are added, and the mixture is well shaken. Some of the water layer is withdrawn by a pipette and tested with a solution of benzidine in acetic acid. A blue coloration denotes the presence of either manganese or cobalt.⁵² In the presence of cobalt it is advisable to incinerate the varnish, treat with hot hydrochloric acid, filter, and neutralise carefully with sodium hydroxide solution. It is recommended that the solution be warmed before the addition of the alkali, but the excess of alkali must only be removed when the solution is cold. If manganese be present, a red colour is produced on addition of a solution of potassium oxalate, which is said to be due to the formation of $K_2Mn(C_2O_4)_3 \cdot 3H_2O$.⁵³ It is stated that 0.012 milligram of manganese can be detected in 10 c.c. of solution even in the presence of lead and cobalt. A modification of the method has been put forward by P. H. Herman,⁵⁴ in which the varnish is incinerated and the ash is dissolved in hydrochloric acid. The solution is boiled for a few minutes to expel chlorine, and excess of potassium hydroxide added to remove the free acid. The turbid solution is cleared by addition of oxalic acid, and a solution of sodium nitrate, followed by a few drops of hydrogen peroxide, gives a currant-red coloration if manganese be present. It is possible to detect manganese in the presence of cobalt without incineration of the varnish or oil by a modification of Crum's manganese test. 2-3 c.c. of the varnish are thinned with 3-4 c.c. of light petroleum and shaken for six to eight minutes

with moderately dilute nitric acid. The aqueous layer is withdrawn and boiled with manganese-free lead peroxide, and a violet colour shows the presence of manganese.

Manganese in the ash of a varnish may be estimated by the usual methods (for details of the bismuthate method see W. W. Scott, *Standard Methods of Chemical Analysis*, 1917, p. 629).

Cobalt.—As in the detection of manganese, the varnish may be examined directly or incinerated and the ash tested. If the varnish be diluted with petroleum or benzol and shaken with a weak lemon-yellow coloured solution of α -nitroso- β -naphthol in glacial acetic acid, a red colour is shown in the presence of cobalt. If β -nitroso- α -naphthol be used, the reaction is more sensitive; 0.000059 milligram in 1 c.c. of solution gives a pale red colour, whilst α -nitroso- β -naphthol requires a concentration of 0.00059 milligram per c.c.⁵⁵ If the varnish be incinerated and the ash dissolved in a mineral acid, the addition of ammonium sulphocyanate in excess, with a little concentrated potassium acetate and 2 or 3 drops of saturated tartaric acid (to remove ferric sulphocyanate), will give a blue coloration in the presence of cobalt, due to the formation of $\text{Co}(\text{ONS})_4(\text{NH}_4)_2$.

The test may be performed without incineration of the varnish. Shake the varnish, previously diluted with light petroleum, with dilute hydrochloric acid, separate the water layer, and examine it as above. If rosin be present the procedure is slightly modified. 1.5 c.c. of thinned varnish is shaken with $\frac{1}{2}$ c.c. of ammonium cyanate solution; $\frac{1}{4}$ c.c. amyl alcohol and 3-4 c.c. ether are added, and the mixture shaken. As a red colour might indicate a trace of iron, 1 c.c. of ammonium acetate solution and 2-3 drops of a saturated solution of tartaric acid are added, whereby the varnish-ether-amyl-alcohol layer becomes green. The addition of 1 c.c. acetone causes the cobalt blue colour to appear in the aqueous layer. This test works even in the presence of lead and manganese.

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